THE JOURNAL
OF
CHEMICAL PHYSICS

VOLUME 8 NOVEMBER, 1940 NUMBER 11

Photosensitization and Fluorescence by Aromatic Hydrocarbons

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(Received August 7, 1940)

Benzene, naphthalene, related hydrocarbons and some of their derivatives act as optical sensitizers towards the decomposition of alkyl iodides in hexane solution. Within this group, the sensitizing power of a substance towards an acceptor runs parallel with the ability of the acceptor to quench the fluorescence of the sensitizer; this is demonstrated quantitatively and in detail. The quantum yield of the naphthalene-sensitized decomposition of ethyl iodide follows an equation of the form $1/\Phi = a + b(1/[\mathrm{EtI}])$, and detailed analysis of the quenching and sensitization shows that while sensitization and fluorescence are alternative processes, they are not completely reciprocal, in that more molecules may sensitize than may potentially fluoresce. All of the observed features of the sensitization are consistent with its being the result of a resonative transfer of energy at collision from the excited sensitizer to the acceptor.

WHILE the capacity of certain dyes to initiate chemical reaction in other substances under the influence of the light absorbed by the dye has long been known, no systematic attention seems hitherto to have been given to the investigation of possible photosensitizing actions of the simpler organic molecules. It is true that several well-investigated photolyses might be termed "internal photosensitizations" in the sense that the bond broken is located in a different part of the molecule from that primarily concerned in the interaction of the photon, as, for instance, in the decomposition of aldehydes and ketones; but cases of transfer of electronic energy from rather simple organic molecules to other molecules have only incidentally been observed. One of the first explicit records of photosensitization by a simple organic molecule was that of the rearrangement of ortho-nitroso-benzaldehyde to the nitro-benzoic acid, in acetone solution, which proceeds with undiminished yield in spectral regions in which the bulk of the absorption is by the acetone, as compared with the yield in regions where the aromatic compound absorbs practically all the light.[1] A similar phenomenon is shown in ethyl iodide dissolved in benzene, or in methyl iodide,[2,3] and it is particularly interesting that this type of photosensitization by solvents can occur, as in the reaction examined by Weigert and Pruckner,[1] and in the photolysis of ethyl iodide dissolved in methyl iodide, in solvents which are themselves capable of photolysis at the wavelengths at which they sensitize. Such sensitizers must either be subject to a certain delay between the absorption of a photon and the disruption of the bond ultimately affected, long enough to allow the excited molecule to make at least one collision with the acceptor, or the primary disruption is largely reversible without

[1] F. Weigert and F. Pruckner, Zeits. f. physik. Chemie, Bodenstein Festband, 775 (1931).
[2] W. West and B. Paul, Trans. Faraday Soc. **28**, 688 (1932).
[3] W. West and J. Fitelson, J. Am. Chem. Soc. in press.

degradation of electronic energy until a collision with a solute molecule occurs.[3]

All solvents which absorb light in the same region as a dissolved photolyte do not efficiently sensitize photolysis. Inner filter actions of absorbing solvents undoubtedly exist, as is shown, for example, by the low quantum yields in the decomposition of ethyl iodide in carbon disulphide, (a competing photolyte) or in chlorobenzene, both of which absorb in the same spectral region as the iodide.[3] Nevertheless, even in these cases, the decomposition of the iodide is greater than would be caused by the light absorbed by itself, as determined by its concentration and absorption coefficient.

In all the cases of solvent sensitization mentioned, the absorption bands of the sensitizer and of the acceptor are in the same spectral region, so that the practically and theoretically interesting feature of extension of the photoeffective region of the spectrum to wave-lengths unabsorbed or only slightly absorbed by the photolyte, as is so well exhibited in the sensitization of the photographic plate to red and infra-red light, is not realized. Naphthalene, however, has an absorption spectrum of the same general type as that of benzene, but displaced to longer wave-lengths, where the absorption coefficient of ethyl iodide is very low; preliminary experiments showed a marked acceleration of the rate of decomposition of ethyl iodide in hexane solution containing naphthalene exposed to light near the beginning of the naphthalene absorption spectrum, as compared with the decomposition under identical conditions without the naphthalene. The study of the photolysis of ethyl iodide in presence of naphthalene, and related measurements on the fluorescence and extinction of fluorescence of naphthalene, form the subject matter of this paper. It may be said at once that the essential conclusion of the study is that the reaction is a true sensitized decomposition of the ethyl iodide molecule by resonative transfer of energy on collision with an electronically excited naphthalene molecule in a process which seems, in the main, free from further complication.

General Scheme for Fluorescence and Photosensitization

The existence of an intimate relation between the capacity of a substance to fluoresce, or, more precisely, to exhibit fluorescence extinguishable by the addition of a foreign substance, and its ability to act as a photosensitizer towards the substance is obvious immediately in terms of our present understanding of molecular excitation. The existence of fluorescence in a substance shows, at least, that all of its molecules do not dissipate all of their electronic energy chemically in themselves or in internal or external degradation, and the substance must therefore be potentially able, under suitable conditions, to transfer electronic energy, as such, to acceptors. Fluorescent substances must, therefore, always be potential sensitizers. But experimentally, it is well known that photosensitization can be effected by substances that do not fluoresce,* as in Eder's reaction in the presence of ferric ion, and we have to envisage the possibility, in complex molecules, that a greater number of excited molecules is capable of producing sensitization than, in the absence of the acceptor, would produce fluorescence. There are, no doubt, various mechanisms by which this might arise, but for the sake of concreteness, we shall suggest one which may be relevant to the cases examined here.

According to measurements of Bowen,[4] the quantum yield of fluorescence of naphthalene is about 0.2, in solution. Now, while it is possible that the low yield is due to dissipation of electronic energy on collision with the solvent, it seems more likely, in view of the inertness of hexane, that the naphthalene in solution is inherently unable to emit a photon more often than about once in five excitations. The excited electronic level in naphthalene from which the fluorescence starts, is very probably (as the apparently corresponding level in benzene is known to be)[5] capable of combining radiatively

* We are, of course, discussing sensitizations effected by more or less direct transfer of electronic energy from the sensitizer to the acceptor; processes like those often induced by chlorine, which appear to depend on the initiation of atomic chain reactions by the illuminated sensitizer, are here irrelevant.

[4] E. J. Bowen, Trans. Faraday Soc. **35**, 16 (1939).

[5] A. L. Sklar, J. Chem. Phys. **5**, 669 (1937); H. Sponer, G. Nordheim, A. L. Sklar and E. Teller, *ibid.* **7**, 207 (1939).

with the normal state only by the simultaneous excitation of certain asymmetric vibrations. Transitions to vibrational states of other symmetry could not occur with fluorescence; but such transitions are not prohibited at collision, and, under suitable conditions, could cause photosensitization. In such a case, quenching of fluorescence by the acceptor, and sensitization by the excited molecule would not be completely identical processes; sensitization could be effected by molecules, which, left to themselves, would not fluoresce.

It may facilitate discussion of some of the experiments to set down here the equations for the dependence of fluorescence extinction and of sensitization on the concentration of acceptor, for the two cases, (A) of complete equivalence of quenching and sensitization, and (*B*) for the case in which excited molecules of sensitizer may sensitize without being potentially capable of fluorescing.

In the following scheme for case (*A*), N is the fluorescing or sensitizing molecule, S the acceptor and S^* the products of the sensitized reaction.

(*A*)	$N+h\nu_1=N^*$		absorption
	$N^*=N$	k_i	deactivation
	$N^*=N+h\nu_2$	k_f	fluorescence
	$N^*+S=N+S^*$	k_s	sensitization

The stationary concentration of N^* is $[N^*]=I_{abs}/(k_i+k_f+k_s[S])$ where I_{abs} is the intensity of the light absorbed; the intensity of fluorescence is given by the Stern-Volmer equation

$$I=\frac{k_f I_{abs}}{k_i+k_f+k_s[S]}. \tag{1}$$

The quenching function, the ratio of the unquenched to the quenched fluorescence intensity, becomes

$$I_0/I=1+k_s[S]/(k_i+k_f), \tag{2}$$

i.e., the quenching function is linear in the concentration of quencher, with a slope, the quenching constant, $k_q=k_s/(k_i+k_f)$. The concentration of quencher which reduces the intensity of fluorescence to half its unquenched value is

$$[S]_{\frac{1}{2}}=(k_i+k_f)/k_s. \tag{3}$$

The equation for the rate of sensitization, $=k_s[N^*][S]$ leads to the expression for the quantum yield for sensitization

$$\Phi_s=\frac{[S]}{(k_i+k_f)/k_s+[S]}$$

or

$$\frac{1}{\Phi_s}=\left(\frac{k_i+k_f}{k_s}\right)\cdot\frac{1}{[S]}+1, \tag{4}$$

i.e., the sensitization function $1/\Phi_s$ is linear in $1/[S]$ and its slope is the reciprocal of that of the quenching function. At high concentrations of sensitizer, Φ_s approaches the limiting value of 1, and the concentration of sensitizer at which the sensitized yield has half its limiting value is

$$[S]_{\frac{1}{2}}=(k_i+k_f)/k_s, \tag{5}$$

the same as for the quenching of fluorescence.

In case (*B*), two types of activated N are assumed, N^* which may fluoresce or sensitize, and N^{**} which can sensitize, but not fluoresce.

(*B*)	$N+h\nu_1=N^*$		absorption
	$N^*=N$	k_{i_1}	deactivation
	$N^*=N^{**}$	k_{i_2}	deactivation for fluorescence but not for sensitization
	$N^*=N+h\nu_2$	k_f	fluorescence
	$N^*+S=N+S^*$	k_{s_1}	sensitization
	$N^{**}+S=N+S^*$	k_{s_2}	sensitization
	$N^{**}=N$	k^*	deactivation of N^{**}

The stationary concentrations of N^* and N^{**} are

$$[N^*]=\frac{I_{abs}}{a+k_{s_1}[S]} \quad \text{where} \quad a=k_{i1}+k_{i2}+k_f$$

and

$$[N^{**}]=\frac{k_{i2}[N^*]}{k^*+k_{s2}[S]}.$$

The fluorescence function becomes

$$I_0/I=1+k_{s1}[S]/a \tag{6}$$

and the concentration of quencher for half-quenching is

$$[S]_{\frac{1}{2}}=a/k_{s1}. \tag{7}$$

The quantum yield for sensitization becomes

$$\Phi_s=\frac{(k^*k_{s1}+k_{i1}k_{s2})[S]+k_{s1}k_{s2}[S]^2}{(ak_{s2}+k^*k_{s1})[S]+k_{s1}k_{s2}[S]^2+ak^*},$$

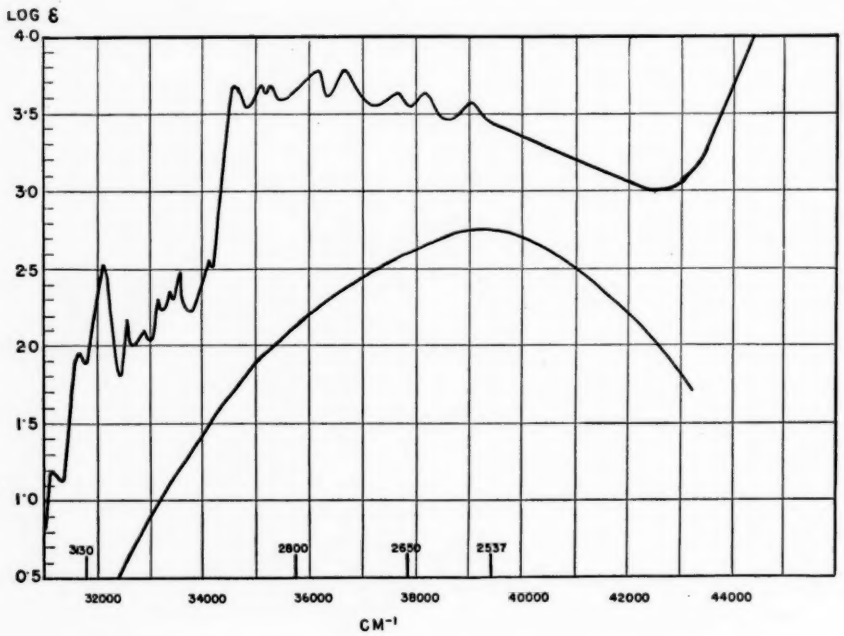

FIG. 1. Absorption of naphthalene and of ethyl iodide.

which, neglecting terms in $[S]^2$, assumes the form

$$\Phi_s=\frac{A[S]}{B[S]+C}, \tag{8}$$

where

$$A=k^*k_{s1}+k_{i_2}k_{s_2}, \quad B=ak_{s_2}+k^*k_{s_1}, \quad C=ak^*.$$

The reciprocal of the yield is

$$\frac{1}{\Phi_s}=\frac{C}{A}\cdot\frac{1}{[S]}+\frac{B}{A}, \tag{9}$$

i.e., the sensitization function is still linear in $1/[S]$, to the extent that terms in $[S]^2$ can be neglected. The slope of the sensitization function is no longer equal to the reciprocal of that of the quenching function, but assuming $k_{s_1}=k_{s_2}$, becomes equal to this reciprocal multiplied by $1/(1+k_{i_2}/k^*)$, i.e., is smaller than the reciprocal of the quenching function. The concentration of S at which the sensitized yield is reduced to half its limiting value is also smaller than that for reducing the intensity of fluorescence to half its unquenched value.

Additivity of the Absorption Spectra of Naphthalene-Ethyl Iodide Mixtures

The absorption spectra of naphthalene and of many of its derivatives have been measured by Victor Henri and de László.[6] Between about wave-length 3200A and 2900A, a series of well-defined sharp bands is observed in the parent hydrocarbon, with maximum extinction coefficients, in hexane, of about 100, and with all the appearance of bands associated with an electronic transition between two stable states. This is followed, between 2800A and 2500A, by a region of much more intense absorption ($\epsilon=2000$ to 5000) in which the maxima have the diffuse appearance of predissociation bands. This type of absorption is observed both in the vapor and in solution, the main difference being a relatively small shift of the bands to long wave-lengths in hexane. The derivatives show the same type of absorption, although the intensity is usually greatly increased over that of naphthalene in the first region, and sometimes both regions are diffuse.

Ethyl iodide in hexane solution, as reported by Scheibe[7] and checked quantitatively in this investigation, shows a broad structureless absorption band, stretching from about 3200A to about 2300A, with a maximum at about 2600A. Figure 1 shows the relation between the absorption spectra of the two substances, for which the

[6] V. Henri and H. de László, Proc. Roy. Soc. **A105**, 662 (1924); H. de László, *ibid.* **111**, 355 (1926).
[7] G. Scheibe, Ber. **58**, 592 (1925).

data for naphthalene have been taken from the work of Henri and de László, and for ethyl iodide from our own measurements.

In general, the transfer of energy which initiates a sensitized photolysis might occur in the excited state of a long-lived complex formed from the sensitizer and acceptor, or in the process of collision between the excited sensitizer and the acceptor. The former mechanism would almost certainly lead to changes in position and intensity of the absorption spectrum of a mixture of sensitizer and acceptor as compared with those of the components, while the collision mechanism would produce changes quite inappreciable to the routine methods of photometry, under ordinary conditions of concentration and intensity of illumination. We have, therefore, carried out measurements of the absorption coefficients of mixtures of naphthalene and ethyl iodide in hexane solution, using the method of H. Stücklen.[8] This method is based on measurements of the wave-lengths of cut-off of the unknown and of a standard substance of known concentration, thickness and absorption coefficient, and depends for its validity on a fortunate accident with respect to the variation of sensitivity of the photographic plate on the one hand and of the spectral distribution of intensity of the continuous hydrogen emission on the other; nevertheless we have found it to give results, in a number of tests on known substances, of the same accuracy as the much more laborious method using calibrated screens. The result of the measurements on the naphthalene-ethyl iodide mixtures is that the light absorbed by mixtures in the concentration range 0.01 to $0.001M$ naphthalene and $0.01M$ ethyl iodide in hexane is simply the sum of that absorbed by the components separately. The conclusion is that in that concentration range (that used in the photo-experiments) no long-lived complex exists between ethyl iodide and naphthalene, and that any transfer of energy between these molecules must take place at collision.

Preliminary Sensitization Experiments

The first orienting experiments were performed very simply, by exposing together test tubes, filled with solutions of ethyl iodide in hexane, with and without the sensitizer, to the same intensity of light from a quartz mercury lamp, and comparing the depth of color of iodine produced in the two cases. Air was removed from the tubes by the passage of a current of nitrogen, carefully freed from oxygen, for some time before the exposures. Table I contains a list of the substances examined, arranged roughly in the order of their sensitizing action towards ethyl iodide.

Fluorescence of Naphthalene and its Quenching by Ethyl Iodide

For the reasons already discussed, we have carried out, parallel to the photo-experiments, a study of the fluorescence of naphthalene and certain of its derivatives, and particularly of its quenching by ethyl iodide. The fluorescence spectrum of naphthalene has long been known to consist of a series of bands on the long wave side of the first absorption region,[9] and as our own observations on the fluorescent yield (i.e., the number of fluorescent quanta emitted per quantum absorbed) in naphthalene as a function of the exciting wave-length, although apparently not recorded in the previous literature, are quite typical of this class of phenomena in solution, as demonstrated particularly by the work of Vavilov[10] and of Pringsheim,[11] no lengthy description of the experimental arrangements seems necessary. Light from a General Electric capillary mercury arc, type H3, from which the glass envelope had been removed,

Table I.

Best Sensitizers	Less Efficient	Inhibitors
Naphthalene	α-naphthol	α-chlornaphthalene
Acenaphthene	β-naphthol	α-nitronaphthalene
Fluorene	α-naphthyl ethyl ether	α-naphthoic acid
	β-naphthyl ethyl ether	anthracene
	α-naphthylamine 4-sulphonic acid	
	1-nitro 2-naphthylamine	
	β-naphthonitrile	
	α-naphthonitrile	

[8] H. Stücklen, J. Opt. Soc. Am. **29**, 37 (1939).

[9] E. Dickson, Zeits. f. wiss. Phot. **10**, 166, 181 (1912).

[10] S. I. Vavilov, Zeits. f. Physik **22**, 266 (1924).

[11] P. Pringsheim, Trans. Faraday Soc. **35**, 28 (1939).

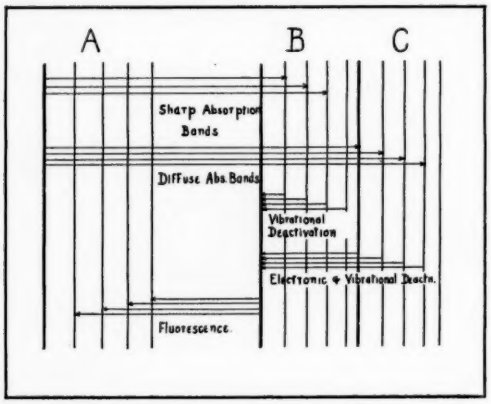

FIG. 2. Energy levels in naphthalene (schematic).

was passed through a quartz monochromator, and the isolated lines used to excite fluorescence in the naphthalene solution, placed in a small quartz cell at the exit slit. The fluorescent spectrum was photographed by means of the small Hilger quartz spectrograph. The relative intensities of the mercury lines as they issued from the monochromator were determined by a thermopile and galvanometer. Concentrations of naphthalene solutions used for the different exciting wave-lengths, were so chosen, with the use of de László's values of the absorption coefficients,[6] that in all cases 90 percent absorption of the incident light occurred in a 5-mm layer of solution, and the times of exposure to the different exciting lines so made, that the same number of photons entered the solution during the exposure. The shortest exposure was 20 min. and since the different intensities of the mercury lines caused the exposures, all made on the same photographic plate, to vary over a factor of eightfold, a rough correction for the lack of photographic reciprocity between intensity and time was made from the data given in the Eastman Kodak pamphlet on photographic plates.[12] The concentrations of naphthalene for the different exciting wave-lengths varied from 2.5×10^{-2} M to 4.5×10^{-4} M, but there seems little self-quenching at the highest of these concentrations, and it is valid to compare among themselves the fluorescent intensities excited by different wave-lengths.

[12] *Photographic Plates for Use in Spectroscopy and Astronomy*, Third Edition (Eastman Kodak Company, Rochester, New York, 1937), p. 12.

The spectra photographed in this way by excitation by the wave-lengths 3130, 3030, 2650 and 2537A were identical in features, and the photographic densities were practically the same. Of these wave-lengths, 3130 and 3030A are in the region of sharp absorption of the naphthalene, the others in the predissociation region, and the conclusion is that between exciting wave-lengths 3130 and 2537A, the quantum yield of fluorescence is substantially independent of wave-length, whether in the sharp or diffuse region of absorption.

The absorption spectrum of naphthalene (Fig. 1) shows that three electronic levels are concerned in the fluorescence and photosensitizations studied here; the normal level A, the upper level associated with the sharp absorption bands, B, and the higher level C associated with the strong diffuse bands (Fig. 2). The independence of the fluorescence in solution on the exciting wave-length points to there being a common initial state for the fluorescent emission, independent of the vibrational state reached as the result of absorption; a molecule excited to a high vibrational level in B is deactivated without radiation to the lowest vibrational state in B, and it is the stability of the electronic state B itself towards deactivating processes at collision that allows the electronic transition $B\rightarrow A$ (with appropriate vibrational changes) to occur with fluorescence. On the other hand, a molecule excited to levels associated with the electronic level C is practically certain to undergo a radiationless transition to B, so that excitation even in the region of diffuse absorption produces the same fluorescence as in the region of sharp bands.

This continuation of fluorescence, with undiminished yield, on extension of the exciting radiation into a region of "predissociation" in solution has previously been observed and commented on by Terenin, Vartanian and Neposent in hexane solutions of aniline.[13] The phenomenon is of general interest in the photochemistry of liquids and solutions, as it is proof that no general dissociation need occur in the liquid state, even though the spectrum suggests predissociation, and diminished fluorescence in

[13] A. Terenin, A. Vartanian and B. Neposent, Trans. Faraday Soc. **35**, 39 (1939).

the gas indicates dissociation in this phase. Fluorescence on excitation in a predissociation region in the liquid state may be the most direct proof of the reality of the phenomenon of primary recombination of Franck and Rabinowitch.[14]

Quenching of fluorescence of naphthalene by ethyl iodide

These experiments were performed to ascertain to what extent the reciprocal relations demanded by mechanisms (*A*) and (*B*) were, in fact, fulfilled. It may be said at once that the results were entirely in accord with a general mechanism of energy transfer from sensitizer to acceptor at collision.

The fluorescence was measured by means of a potassium photoelectric cell of the vacuum type and an "electrometer tube" circuit using the General Electric tube FP-54. The balanced circuit of DuBridge and Brown was used, and the circuit constants given by A. E. Whitford[15] were found to function well without modification. Light from a capillary quartz arc, rendered monochromatic (3130A) by the use of the Corning filter No. 986A and dilute chromate solution, was focused on the quartz cell containing the fluorescent solution. The cell was blackened except for entrance and exit slits, on faces perpendicular to each other, the fluorescent light being measured at right angles to the incident. The entrance window of the case containing the photoelectric cell and amplifying tube was placed as close as possible to the exit window of the fluorescence cell. This entrance window was a piece of fluorescent uranium glass, about 6 mm thick, which by its conversion of the ultraviolet fluorescence of the naphthalene solution into green fluorescent light, affected the glass-enclosed potassium surface of the photo-cell. The photoelectric currents were measured by direct deflection of a Leeds and Northrup galvanometer, type P, with coil resistance of about 1000 ω, and ample sensitivity (deflections of about 150 mm for unquenched fluorescence in naphthalene, which has a fluorescence efficiency of only about 0.2) was secured with a grid resistance of 10^{11} ω.

By weakening, by means of calibrated screens, direct ultraviolet light of wave-length 3660A (a wave-length present in the fluorescent spectrum of naphthalene) of intensity comparable to that of the fluorescent light, it was established that the galvanometer deflections were proportional to the intensity of the light entering the photoelectric cell.

The experimental results are contained in Table II and in Fig. 3. The linear plot of the ratio of the unquenched to the quenched fluorescence intensity, I_0/I, as a function of the concentration of quencher, within the range of concentrations measured, shows that the quenching conforms to Eqs. (2) or (6), $I/I_0=1/(1+k_q[\mathrm{EtI}])$. The quenching constants in the table are the values of k_q in this equation. The concentrations of the fluorescent substances in the experiments summarized in Table II and Fig. 3 were so chosen that 50 percent of the exciting light was absorbed in a 2-cm layer of solution.

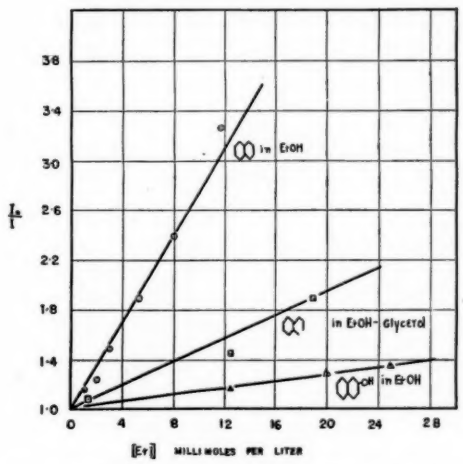

FIG. 3. Quenching of fluorescence of naphthalene compounds by EtI.

TABLE II. *Quenching of fluorescence of some naphthalene derivatives.*

FLUORESCENT SUBSTANCE	CONC. MOLAR	SOLVENT	QUENCHER	k_q LITERS MOLE^{-1}
Naphthalene	1.93×10^{-3}	ethanol 95%	ethyl iodide	180
Naphthalene	1.93×10^{-3}	ethanol-glycerol, 1/1	ethyl iodide	40
Naphthalene	1.93×10^{-3}	ethanol 95%	methyl iodide	230
Naphthalene	1.93×10^{-3}	ethanol 95%	ethyl bromide	<1
Naphthalene	1.93×10^{-3}	ethanol 95%	sodium iodide	2
β-naphthol	1.9×10^{-4}	ethanol 95%	ethyl iodide	14
α-naphthoic acid	2.6×10^{-5}	ethanol 95%	ethyl iodine	<1

[14] J. Franck and E. Rabinowitch, Trans. Faraday Soc. 30, 125 (1934).

[15] J. Strong *et al.*, *Procedures in Experimental Physics* (Prentice Hall, New York, 1939), p. 418.

In a given combination of fluorescing material and quencher, an increase in the viscosity of the medium diminishes the quenching, as is shown by the values of the quenching constant for naphthalene-ethyl iodide in ethanol and in a 1/1 mixture (by volume) of ethanol and glycerol. Also, the quenching efficiency of a given sub stance is greatly dependent on the fluorescent molecule. Whereas an addition of about 0.005 mole per liter of ethyl iodide suppresses the fluorescence of naphthalene to half its value, ten times as much is required to do the same in β-naphthol subject to the same intensity of absorbed light, and α-naphthoic acid and α-chloronaphthalene are affected only by very high concentrations of ethyl iodide. In this connection, in view of the great efficiency of iodide ion in quenching the fluorescence of certain ions, as in quinine bisulphate, uranyl salts, fluorescein and other dyes[16] it may be mentioned that it has little effect on the fluorescence of naphthalene. The quenching constant of sodium iodide towards naphthalene in ethanol is 2.1 liters mole^{-1}, compared with a constant of 180 for ethyl iodide in the same fluorescent system. Methyl iodide shows a high constant towards naphthalene ($k=230$ l. mole^{-1}) while ethyl bromide up to concentrations of 50 millimoles per liter has no quenching effect on this fluorescence.

The parallelism between high quenching of the fluorescence of a naphthalene derivative by ethyl iodide and efficient sensitization of the photolysis of the iodide by the derivative is indicated by a comparison of Tables I and II. β-naphthol, relatively slightly quenched by ethyl iodide, is a less efficient sensitizer than naphthalene, and α-naphthoic acid, quenched only at very high concentrations of the iodide, has practically no sensitizing action. It is to be noticed that the lack of quenching and sensitization in the last two compounds is not connected with low fluorescence; measurements which we hope to report in detail later show that these substances have a considerably higher quantum yield of fluorescence than naphthalene.

TABLE III. *Rates of sensitized and direct photolysis.*

	EXP. A	EXP. B	EXP. C
[Naphthalene]	1.8×10^{-3} M	1.9×10^{-3} M	1.8×10^{-3}
[Ethyl iodide]	2.5×10^{-3}	7.9×10^{-2}	5.0×10^{-3}
$\frac{\text{Sensitized rate}}{\text{Direct rate}}$	3.46	3.34	7.15
$\frac{\text{Total absorption in sens. reaction}}{\text{Total absorption in direct reactn.}}$	3.15	3.20	7.36

[16] E. R. Jette and W. West, Proc. Roy. Soc. **A121**, 299 (1928).

QUANTUM YIELDS IN THE NAPHTHALENE-SENSITIZED PHOTOLYSIS OF ETHYL IODIDE

The apparatus and method of measurement were substantially the same as described previously.[3] Yields have been determined at wave-lengths 3130A, furnished by a mercury arc and Corning filter No. 986A+dilute chromate solution, and at 2537A, from a "resonance arc" at such a distance from the reaction cell that the air-path prevented any appreciable amount of light of wave-length 1849A from reaching the reaction cell. The quantum yields are expressed in terms of the number of iodine atoms produced per total number of quanta absorbed by the reacting system. Iodine was determined photometrically.[3] Precautions to remove oxygen from the reaction cell were taken, but the elaborate arrangements of the former paper were replaced by the simpler and nearly equally effective method of bubbling nitrogen, freed from oxygen by passage over heated copper and then through pyrophoric iron through the solution for half an hour before starting exposure. Moreover since the main aim was to compare relative values of the yields in the direct and in the sensitized photolysis, the lengthy integration process in the energy measurements formerly used was replaced by one in which the light was focused so as to fill the surface of the thermopile. Accurate relative yields can be obtained in this way, and previous values obtained by the more exact absolute method for the direct reaction were used as the basis of the absolute yields reported here.

The unsensitized photolysis of ethyl iodide

The essential characteristics of this reaction in hexane solution are: the iodine yield is always less than unity, 0.3 at wave-length 3130A and

TABLE IV. *Effect of naphthalene concentration.*

[EtI] =0.02*M*	λ=3130A		FRACTION OF LIGHT ABSORBED BY EtI ALONE =0.25				
[Naphthalene]	0.6*M*	8×10^{-2}	1.8×10^{-2}	4.1×10^{-3}	1.8×10^{-3}	9×10^{-4}	1.6×10^{-4}
Percent light abs. in sens. reaction	100	100	100	75	60	57	35
Quantum yield	0.30	0.31	0.31	0.29	0.31	0.31	0.30

TABLE V. *Sensitized yield as a function of* [EtI].

[NAPHTHALENE] =0.0018*M*						FRACTION OF λ3130A ABSORBED BY NAPHTHALENE, 0.55 FRACTION OF λ2537A ABSORBED BY NAPHTHALENE, 1.0					
[EtI]*M*	1.10	0.13	0.079	0.052	0.046	0.024	0.021	0.018	0.014	0.0062	0.0060
Φ_{3130}	0.32	0.31	0.31	0.30	0.33		0.30	0.30	0.31	0.27	0.25
Φ_{2537}						0.41			0.38		
[EtI]	0.0050	0.0043	0.0011	0.00084	0.00047	0.00021	0.000025				
Φ_{3130}	0.27		0.15			0.075	0.051				
Φ_{2537}	0.24	0.24		0.16	0.092						

0.41 at 2537A, independent of the iodide concentration down to a few thousandths molar, and of the light intensity over at least a moderate range. The primary process seems to be a dissociation into iodine atoms and ethyl radicals, and the deficiency of the quantum yield from unity seems largely due to recombination of the radical and the iodine atom.[2,3]

Rates of sensitized and unsensitized reactions

Table III illustrates the influence of naphthalene in accelerating the rate of production of iodine from ethyl iodide in hexane at wave-length 3130A and constant light intensity. The increase in the rate of decomposition of the iodide is directly proportional to the increased absorption caused by the sensitizer; in the presence of the naphthalene, all of the light absorbed is available for the decomposition of the iodide, which proceeds at the rate which it would have done if the iodide itself had absorbed all the light.

Effect of concentration of naphthalene

The effect of varying the concentration of sensitizer at constant concentration of the iodide is shown in Table IV. The over-all quantum yield is independent of the naphthalene concentration, and has the same value at 3130A, within the limits of experimental error, as the unsensitized yield. At very low concentration of the naphthalene the light is mostly absorbed by the iodide, which decomposes by the unsensitized reaction; at higher naphthalene concentrations, the sensitizer absorbs most of the light, and the decomposition is effected by sensitization. The identity of yield for the two processes shows that once the energy has been acquired by the ethyl iodide molecule, whether directly from a photon of wave-length 3130A or from a naphthalene molecule previously excited by such a photon, the subsequent processes are the same. The ethyl iodide dissociates, and the secondary reactions, which are the processes that determine the experimental yield, are the same, irrespective of the manner in which the photolyte molecule obtains its electronic energy.

Effect of ethyl iodide concentration

Above iodide concentrations of about 0.01*M*, the sensitized yield is independent of the concentration of photolyte, but a very distinct decrease in the sensitized yield sets in below that concentration (Table V and Fig. 4). The linear relation between $1/\Phi$ and $1/[EtI]$ demanded by Eqs. (4) and (9) is fulfilled within the experimental error of about 5 percent in a determination of Φ (Fig. 5). Within this limit, too, the sensitized yields at 3130A and 2537A are the same; the limiting values of the yields at high concentrations are, of course, different at these wave-lengths, as these are the yields in the direct photolysis. From the equation of the line in Fig. 5, $1/\Phi=3.2+0.0035(1/[EtI])$, the curve for Φ as a function of [EtI] in Fig. 4 has been drawn, and is seen, except at very low concen-

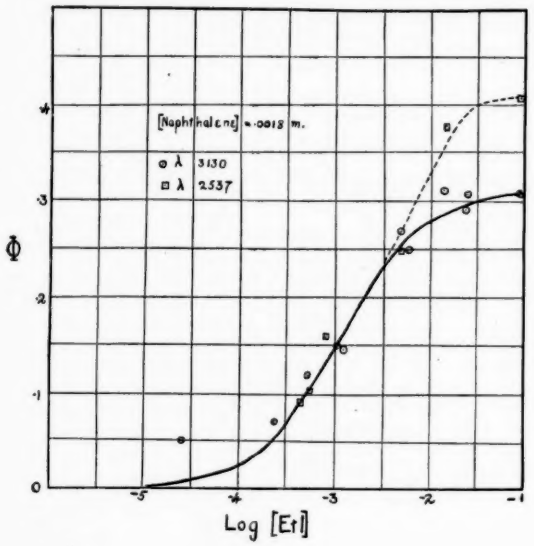

FIG. 4.

trations, where the small amounts of iodine produced and the length of the experiments impose low precision in the measurements, to be in accord with the experimental data.

The slope of the sensitization function, 0.0035, is smaller than the reciprocal of that of the quenching function, 0.0057, in agreement with the type of mechanism in scheme (*B*). However, the quenching function has been determined in ethanol solution, while the sensitization experiments have been performed in hexane; but any doubt that the processes of sensitization and quenching follow scheme (*B*) is allayed by a comparison of the magnitudes of the fluorescence yield and of the limiting values of the sensitization yield at high iodide concentration. Bowen's value of the fluorescence yield in hexane is 0.2,[4] (a value which our own preliminary comparative measurements of the fluorescence yields in naphthalene and a number of its substituents suggest is a little high), distinctly smaller than the limiting value of the sensitization yield at wave-length 3130A, 0.3. Moreover, as already mentioned, the defect of this value of the sensitization yield from unity is very probably not due in any great degree to inefficiency in the primary sensitization process, but rather to recombination reactions after the completion of the transfer of energy. There is no doubt then that the sensitization efficiency is considerably greater than the fluorescence efficiency, and more molecules can sensitize than can potentially fluoresce in hexane solution.

Effect of exciting wave-length on sensitization

While the direct photolysis of ethyl iodide takes place at wave-length 2537A with appreciably greater yield than at 3130A, the sensitized yields at these wave-lengths are, within the limits of experimental precision, the same. This fact is easily understood in terms of the mechanism of excitation and fluorescence of naphthalene already adduced; rapid vibrational deactivation to the lowest level of the excited electronic state, *B* (Fig. 2), takes place, and molecules in this state are responsible for practically all the fluorescence and sensitization. The sensitization yield, like the fluorescence yield, is, therefore, independent of the exciting wave-length. Moreover, if a naphthalene molecule, excited by absorption of wave-length 2537A, should collide with an ethyl iodide molecule before deactivation to the common initial level *B* has occurred, the considerations of the following section show that the efficiency of resonance transfers of energy would be less for those excited molecules than for those excited by absorption of wave-length 3130A.

MECHANISM OF QUENCHING AND PHOTOSENSITIZATION

All of the results of the analysis of this reaction are consistent with this essential scheme: optically excited naphthalene molecules disap-

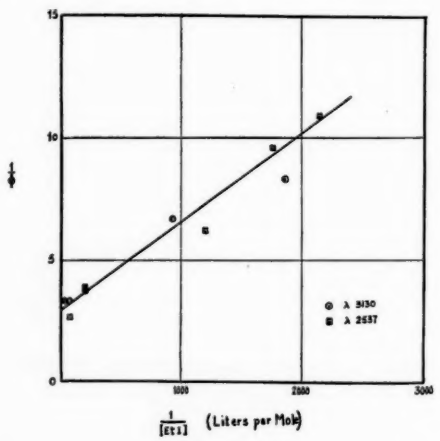

FIG. 5.

pear in the competing processes of fluorescence, photosensitization and internal dissipation of electronic energy. (Transfer of energy to the solvent may also occur, but this factor will be constant in a given solvent.) That the transfer of the electronic energy of the naphthalene takes place at collision is made certain, both by the additivity of absorption by mixtures of naphthalene and ethyl iodide, and by the suppression of quenching and of sensitization in media of high viscosity. (Only preliminary experiments on the effect of viscosity on sensitization have yet been performed, but we have established qualitatively that the sensitization yield in this reaction in Nujol is considerably less than in hexane.) An increase in viscosity will increase the average time required by a potentially quenching solute molecule to diffuse up to an excited molecule and therefore will present the latter a greater chance to radiate before an effective collision can be made. An increase in viscosity can also be expected to increase the duration of a collision once it has occurred, allowing the interacting wave functions longer time in which to set up high amplitude of the resonating condition and therefore facilitate the transfer of energy. With efficient quenchers, however, we must suppose that this occurs with high probability within the collision period in media of low viscosity, so that the net effect of an increase on viscosity is a diminution of quenching and sensitization, other conditions remaining the same. Rabinowitch and Wood[17] have called attention to the role of the viscosity of the medium in reactions taking place with high probability at the first collision, i.e., with very low energy of activation, and the viscosity effects observed here in quenching and sensitization are evidence for a very low energy of activation for these processes.

In the direct photolysis of ethyl iodide, the primary process is very likely a disruption of the molecule to an ethyl radical and an iodine atom. This takes place with highest probability under the influence of photons of wave-length about 2600A, the maximum of absorption, and is relatively improbable at 3130A, to which only ethyl iodide molecules in high vibrational states

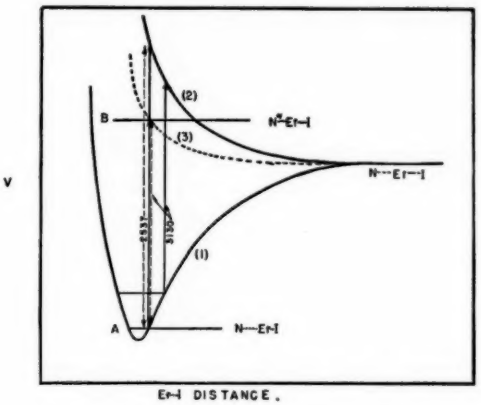

FIG. 6. Mechanism of photosensitization.

can respond. In order to explain the increase in rate of the decomposition of ethyl iodide at wave-length 3130A, we have to see how it is that ethyl iodide molecules in the lower vibrational states can accept from an excited naphthalene molecule just the same amount of energy that they are unable to take up with any high probability from radiation.

The gist of the answer can be seen in the somewhat oversimplified diagram of Fig. 6. Curve (1) is the potential energy curve for Et—I in the normal electronic state with a naphthalene molecule an infinite distance off. The interaction of normal naphthalene and normal ethyl iodide is small, and curve (1) will be only slightly changed as a naphthalene molecule approaches to the collision distance: i.e., the line *A* represents approximately the energy of the configuration N—Et—I at collision. Curve (2) is the repulsive state of ethyl iodide with a normal naphthalene molecule at infinity. An electronically excited naphthalene molecule, however, exerts attractive forces on ethyl iodide molecules, and at the collision distance of such a molecule with ethyl iodide, curve (2) is lowered to (3), the line *B* representing the energy of the configuration N*—Et—I at collision. *A*—*B* represents the electronic transition already referred to as associated with fluorescence, as modified by the colliding ethyl iodide molecule. This transition is undergone by absorption of wave-length somewhere about 3130A, which we shall assume, for simplicity, to be the resonance wave-length. The principle of maximum utilization of elec-

[17] E. Rabinowitch and W. C. Wood, Trans. Faraday Soc. **32**, 1381 (1936).

tronic energy[18] is followed if a resonative transfer for this particular transition occurs, and the net result is that a vibrationally unexcited ethyl iodide molecule, in the process of collision with an excited naphthalene molecule, can now utilize the energy contained in a photon of wave-length 3130A, which it could not absorb directly from radiation.

We can also see how naphthalene molecules excited by wave-length 2537A, would, if they retained the corresponding energy, be less efficient than one excited by wave-length 3130A. Such a molecule on collision with an average molecule of ethyl iodide possesses more energy than is required to raise the iodide to curve (3) by a vertical transition. The excess energy will have to be dissipated as kinetic energy and the process will be less efficient than the one in which the naphthalene has just the correct amount of energy.

Our main object in the present paper has been to demonstrate the phenomenon of optical sensitization by relatively simple organic molecules, and to show that the phenomenon has the features to be expected in one originating in a resonative transfer of energy from sensitizer to acceptor at collision. We are at present engaged in a study of the variation of fluorescence efficiency and sensitizing efficiency in a series of naphthalene and other derivatives, designed to elucidate some of the factors which lead to high sensitizing power, the results of which we hope to present in the near future.

[18] J. Franck and H. Levi, Zeits. f. physik. Chemie **B27**, 409 (1934).

NOVEMBER, 1940 JOURNAL OF CHEMICAL PHYSICS VOLUME 8

On the Kinetics of the Order-Disorder Transformation in Cu_3Au

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(Received August 28, 1940)

Using the elastic modulus S_{11} as an indicator, the rate of the order-disorder transformation of Cu_3Au has been investigated in the region near the critical temperature. The variation of S_{11} with time, at constant temperature, of a [100] single crystal of the alloy has been measured, and all the data for the transformation from disorder to order can be represented in one curve by plotting the fraction of untransformed material against the "reduced" time, t/τ. The relaxation time τ decreases rapidly with increasing amount of undercooling below the critical temperature, and combined with the data of Sykes and Evans on the resistivity *vs.* time curves, points to a minimum in τ about 20°C below the critical temperature. The critical temperature for the ordering process was found to be 386.8°C, for the disordering process 388.0°C. The observed data on the variation of τ with temperature are discussed in terms of a mechanism of nucleation and growth for the transformation.

INTRODUCTION

IN a recent paper[1] the equilibrium elastic moduli of single crystals of Cu_3Au over the temperature range 20°C to 450°C were reported. A discontinuity in the elastic moduli and a narrow temperature hysteresis loop were observed in the neighborhood of the order-disorder critical temperature T_c. The present paper is a report of a more exhaustive investigation of the behavior of the adiabatic elastic modulus S_{11}, in the temperature interval $T_c \pm 15$°C, and of the variation of S_{11} with time at constant temperature, in this interval. The primary purpose of this investigation is the study of the kinetics of the order-disorder transformation. The previous work had shown that S_{11} is a sensitive measure of the state of the alloy, and hence this quantity was used simply as a measure of the process of transformation.

The data here reported were obtained on a

[1] Sidney Siegel, Phys. Rev. **57**, 537 (1940).

single-crystal cylinder of a copper-gold alloy having the composition 75.1 atomic percent copper, 24.9 atomic percent gold. The crystal is one of those on which rigidity modulus measurements had been made in the earlier work. The direction cosines of the cylinder axis with respect to the principal axes of the cubic lattice are 0.9984, 0.0014, and 0.0000. Hence the principal modulus S_{11} of the alloy is equal to $1/E$ for this crystal to 0.2 percent; E is Young's modulus in the cylinder axis direction.

Experimental Details

The method of measuring E is identical with that described before.[1] The crystal cylinder is cemented to an X cut quartz crystal cylinder, and is supported in an evacuated silica tube furnace. Adjacent to the specimen is placed the measuring junction of a Chromel-Alumel thermocouple, imbedded in a metal rod of the same dimensions as the specimen. Figure 1 shows an end and a top view of the set-up.

Three quantities are observed—the resonance frequency of the composite oscillator, the temperature as determined from the e.m.f. of the thermocouple, and the time. From the measured frequency of the composite oscillator, it is possible to calculate the resonance frequency, f, of longitudinal vibration of the specimen crystal cylinder, and from this to obtain Young's modulus E by the relation

$$E=4f^2L^2\rho, \tag{1}$$

where L and ρ are, respectively, the length and density of the specimen at the time and temperature f is measured.

The solid line of Fig. 2 shows the equilibrium values of E plotted against temperature in the region near T_c. The method of taking observations on the kinetics of the ordering, or disordering, process may best be described with the aid of this figure.

For the study of the ordering process, we begin with the alloy in equilibrium at 401°C, with a disordered structure. We indicate this initial state of the material by the point A on the curve. The temperature is now lowered as rapidly as possible by reducing the furnace current to zero. When the furnace has cooled to a temperature T_1, a few degrees below T_c, an automatic control device is put into operation and the furnace stabilized at $T_1\pm0.05$°C. At this time the value of E has risen to the point B. Subsequently frequency measurements are made at known time intervals while the temperature is held constant at T_1, until the alloy is in equilibrium at that temperature, and E has reached its final value, represented by the point C. The temperature is then lowered to 373°C and there maintained until the alloy is in equilibrium, with the

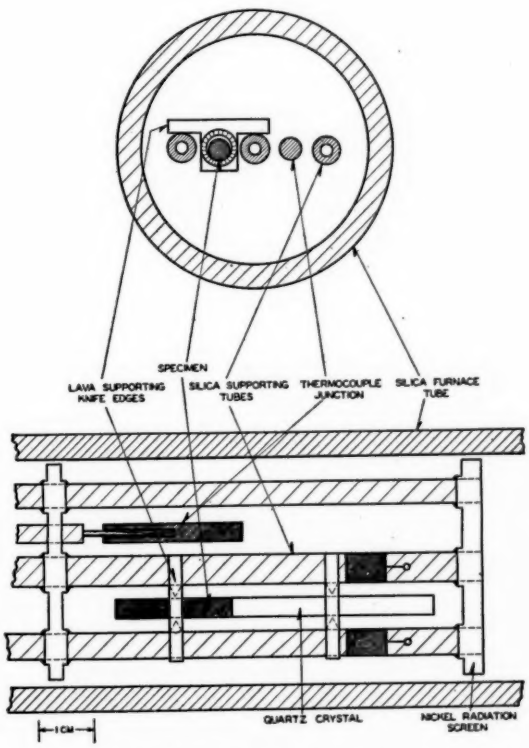

FIG. 1. Top and end view of experimental set-up.

point D representing the value of E at 373°. Finally the material is reheated to 401° and the state represented by the initial point A regained, so that a complete cycle has been traversed. This cycle of operations may now be repeated, with the temperature stabilized at some different value of T_1, below T_c, and another set of data relating time, temperature, and E may be obtained.

The study of the disordering process is completely analogous to that described above for the ordering process. The initial state of the material is now an equilibrium ordered structure at 373°, indicated by the point D of Fig. 2. The tempera-

ture is raised as rapidly as is feasible to a value T_2 above T_c, and stabilized there. At this time the value of E has fallen to the point X. Subsequently frequency measurements are made at known time intervals, while the temperature is held constant at T_2, until the alloy is in equilibrium at that temperature, and E has reached its final value represented by the point Y. The alloy is next heated to 401°C and then slowly cooled to 373°C, until the initial equilibrium

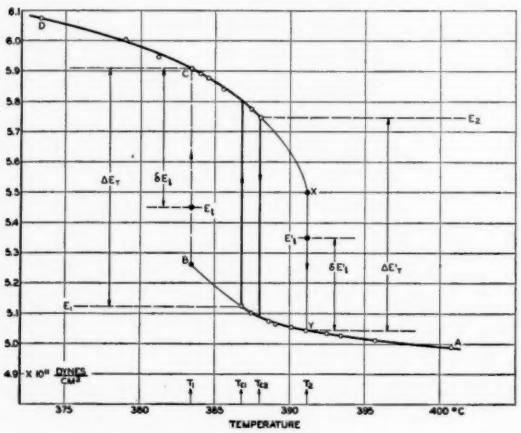

FIG. 2. Equilibrium curve of Young's modulus in the [100] direction of a single crystal of Cu_3Au, plotted against the temperature.

state, represented by D, is regained and a complete cycle has been traversed.

RESULTS

A. Disorder→order

A typical curve of E plotted against time during the ordering process appears in Fig. 3. The points A, B and C of Fig. 2 are indicated here, and the point P indicates the time at which the specimen temperature was equal to the *ordering* critical temperature T_{c1}, 386.8°C. At temperatures higher than T_{c1}, the disordered state is stable, when the initial state of the alloy is a disordered one.

Each of the observed E *vs.* time curves, of which that of Fig. 3 is typical, may be divided into two parts. From the point A to the point B, both E and T were changing with time. From the point B to the final point C, however, T is constant, and E changes with time solely because of the changing degree of order of the lattice. We shall be interested only in this isothermal part of each of the observed curves.

The ideal situation would be one in which the rate of cooling from 386.8°, T_{c1}, to T_1 could be made very rapid, as in a quenching procedure. Then the state of order existing on the lower branch of the equilibrium curve of Fig. 2, at T_{c1}, would be the initial state at T_1, from which the alloy would relax isothermally to its equilibrium degree of order, on the upper branch of the curve at T_1. Each isothermal of E *vs.* time would begin with the initial value E_1 indicated in Fig. 2, and would end with the final value given by the upper equilibrium curve, say the value C at T_1.

For experimental reasons it was not possible to attain this situation, but the data will be treated as if such a condition did actually exist. The assumption is made that the path by which the point B of Fig. 2 is reached will not affect the shape of the isothermal relaxation curve from B to C at the temperature T_1. This assumption appears to be supported by experimental evidence.

We will define a quantity ΔE_T for each temperature T at which an isothermal was run. It is the difference between the value of E in the disordered state at T_{c1}, the quantity E_1, and the value of E in the ordered state at the temperature T. It is evidently the total change in E which would be observed at T_1 if the proposed ideal conditions existed. The quantity ΔE_T for the temperature T_1 is indicated in Fig. 2.

We will define another quantity δE_t. If E_t is the value of Young's modulus at any time t during the isothermal relaxation, and C is the final equilibrium value of E at that temperature, then

$$\delta E_t = C - E_t.$$

The data for the isothermal relaxation from disorder to order at various temperatures were represented by plotting the ratio $\delta E_t/\Delta E_T$ against time. These curves are not exponential decay curves, and no simple function was found that well represented them. The following arbitrary procedure was adopted. The interval Δt between the time that $\delta E_t/\Delta E_T$ was equal to 0.5 and the time that this ratio was equal to 0.25 was found for each curve. We define as the "relaxation

time" of the alloy at a temperature T, the quantity

$$\tau = \Delta t / \ln 2. \quad (2)$$

If the relaxation truly obeyed a law of the form

$$\delta E_t / \Delta E_T = \exp(-t/\tau'), \quad (3)$$

then the quantity τ as defined above would be identical with τ' in the Eq. (3) above.

The isothermals were replotted with $\delta E_t / \Delta E_T$ against the "reduced" time t/τ. It was found that *all* the curves for the isothermal relaxation from disorder to order, when so plotted, could be superposed on *one* curve. This characteristic curve is shown in Fig. 4; the individual curves all fell within the shaded region shown there.

The values of τ obtained in the manner described above, are plotted against temperature in Fig. 5. The critical temperature for the ordering process, above which the disordered state is stable is 386.8°C. The dashed curve shows τ plotted logarithmically against $1/\Delta T$, where ΔT is the difference between 386.8° and the temperature at which the isothermal for τ was obtained.

B. Order→disorder

A typical curve of E plotted against time during the disordering process, appears in Fig. 6. The points D, X and Y of Fig. 2 are indicated here, and the point P indicates the time at which the specimen temperature was equal to the *disordering* critical temperature T_{c2}, 388.0°. At temperatures lower than T_{c2} the ordered state is stable, when the initial state of the alloy is an ordered one.

The data for the transformation from order to disorder are not as simply presented as those for the ordering process. In Fig. 6 there are again two main regions, the portion XY alone corresponding to the isothermal relaxation of the superheated alloy from the ordered to the disordered states.

In a manner analogous to that described above, we define a quantity $\Delta E_T'$ for each temperature T above T_{c2}. If E_2 is the value of Young's modulus in the ordered state just below T_{c2}, and Y is its final equilibrium value at T in the disordered state, then

$$\Delta E_T' = E_2 - Y.$$

Similarly, if E_t' is the value of E at a time t during the relaxation, then we define

$$\delta E_t' = E_t' - Y.$$

The data for the isothermals of the order to disorder process were plotted in the same way as before, but they cannot be reduced to a single "characteristic" curve. The method previously adopted to obtain a relaxation time does not seem plausible here, but it was carried through solely for the sake of comparison. The values of τ were obtained as before from each isothermal, and are plotted against temperature in Fig. 7. The critical temperature for the disordering process, above which the ordered state is stable, is 388.0°C.

Precision of the Data

Three quantities are measured, the resonance frequency of the specimen, the temperature as

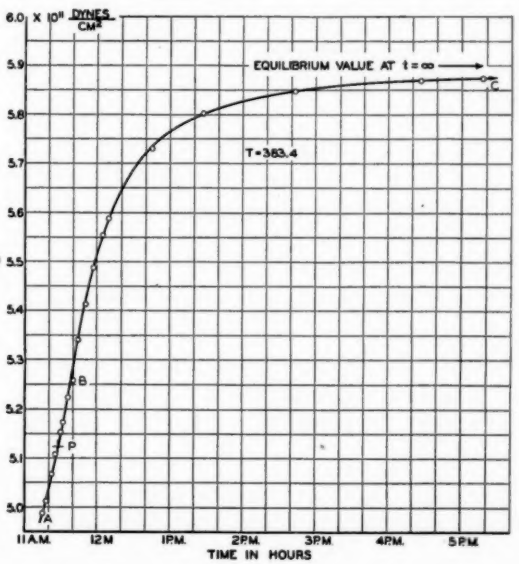

FIG. 3. Typical curve, taken at 383.4°C, of the variation of E with time during relaxation from disorder to order.

determined from the e.m.f. of the thermocouple, and the time. The frequency measurements may be made to 1 cycle in 5×10^4, the e.m.f. to 1 μv in 1.5×10^4, and the time, the independent variable, to 1 second. The main source of uncertainty in the data presented lies in the correlation of these quantities. The furnace temperature may be stabilized to 0.05°C during the isothermal runs, so that the temperature of the thermo-

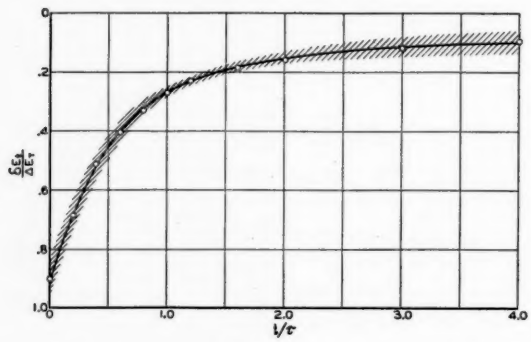

FIG. 4. The "characteristic" transformation curve from the disordered to ordered states.

couple remains constant with time, and the frequency may be measured to 10 cycles as a function of time. The correlation between the temperature of the thermocouple and that of the specimen is not as straightforward as might appear. During most of the runs the measuring junction was imbedded in a copper rod of the same dimensions as the specimen. It was not certain, however, that the temperature of the specimen is the same as that of the copper rod. For the latent heat of transformation of Cu_3Au is reported[2] to be 1.2 calories per gram, and the time required to abstract such an amount of heat per gram of the specimen, with only a few degrees difference between the specimen and the furnace tube, would be of the order of 10 minutes. This time is determined solely by the emissivity of the specimen, the geometry of its surroundings, etc., and is not determined at all by relaxation processes in the material itself.

It was, therefore, felt that although the entire relaxation times observed could not be due simply to the slow rate at which heat is abstracted from the specimen, yet this effect might be large. Check runs were, therefore, made at 381.2°C and at 384.4°C, with the thermocouple junction now imbedded in a rod of Cu_3Au crystal. No difference was found between these curves and the ones previously taken. This fact proves that the times of relaxation observed are to be associated with the ordering process in the material, and are not due to experimental conditions. In the light of these observations it is concluded that the reading of the thermocouple is in fact a measure of the temperature of the specimen, and that this quantity was constant to 0.05°C during an isothermal run.

The last point to be mentioned is the correlation of E for this crystal, which is equal to $1/S_{11}$ for the material, with the frequency. The relationship between E and f expressed in Eq. (1) cannot be applied exactly because of a lack of precise knowledge of L and ρ as functions of T and time in the region near T_c. However, crude measurements of the expansion of Cu_3Au were reported in the previous paper, and these suffice to put an upper limit to the error in E caused by the lack of precise knowledge of L and ρ. The entire effect due to the dilation of the alloy on heating from 375° to 400° is of the order of 0.1 percent; the observed change in E is of the order of 20 percent, so that the maximum error in the *change* in E due to the neglect of the change in L and ρ is only 0.5 percent.

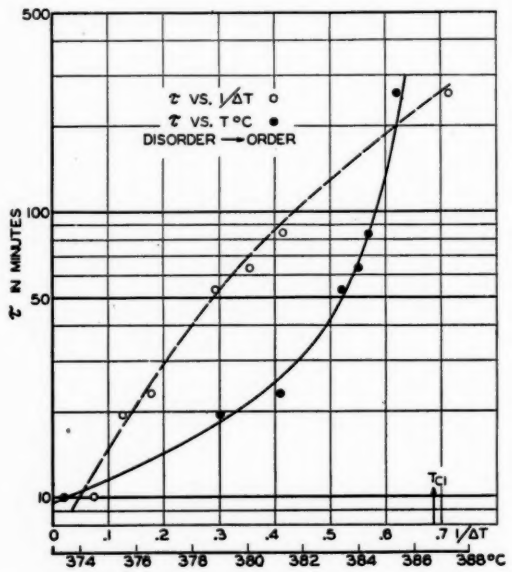

FIG. 5. The variation of the relaxation time τ, plotted against the temperature, and against $1/\Delta T$, for the disorder→order transformation.

The relaxation times as estimated from the isothermals of E *vs.* time vary considerably in fractional error. The smaller values of τ may be in error by as much as 25 percent, the larger values are good to approximately 5 percent.

[2] C. Sykes and F. W. Jones, J. Inst. Metals **59**, 257 (1936).

Discussion of the Results

Bragg and Williams[3] in their original papers discussed the relaxation of the alloy from a state near equilibrium to the equilibrium ordered state. Sykes and Evans[4] measured the variation of electrical resistivity with time for Cu_3Au. Their isothermal resistance-time curves were obtained on polycrystalline specimens, and their method of evaluating the relaxation time τ is different from the present one. Furthermore, the two sets of data for τ were obtained by measurements of different physical properties, but we will assume that they are both in fact measures of the same physical phenomenon, namely the relaxation of the alloy from disorder to order. The data of Sykes and Evans and of the present work are

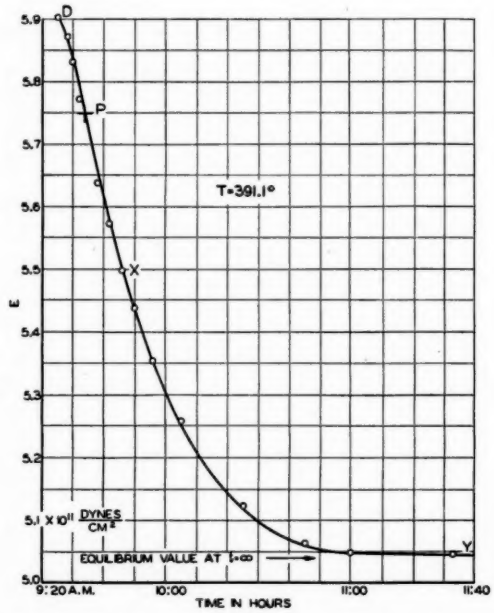

FIG. 6. Typical curve, taken at 391.1°C, of the variation of E with time during relaxation from order to disorder.

shown in Fig. 8, where τ in hours is plotted against the temperature.

The important point to notice is that the variation of τ with temperature, from 340° to 360°, observed by Sykes and Evans, combined with the variation of τ here observed from 375° to T_c, points to the existence of a minimum in the value of τ in the neighborhood of 370°, approximately 20°C below T_c.

It is unfortunate that the two sets of data do not overlap, but for experimental reasons it was not possible to go below 375° without serious modification of the present apparatus and method.

Sykes and Evans postulate that the transformation from disorder to order in Cu_3Au proceeds by the process of formation and growth of nuclei

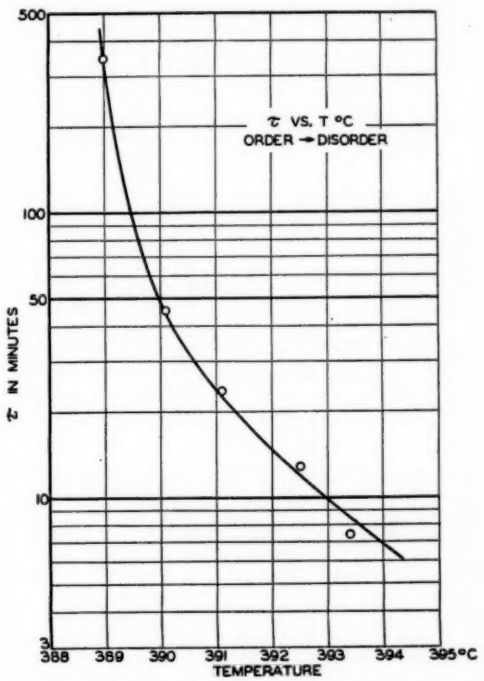

FIG. 7. The variation of τ plotted against the temperature, for the order→disorder transformation.

of order. The results of the present work are in accord with this idea, and add confirmation to it. Such mechanisms of nucleation and growth have been proposed[5] for the description of the kinetics of various kinds of phase changes, and characteristic features of these are the undercooling of the high temperature phase, and the appearance of a maximum in the curve for $1/\tau$ *vs.* T.

Becker[6] has treated the problem of the precipitation of a terminal phase from an undercooled solid solution. He proposes the equation

$$N = Ce^{-[Q+A(T)]/RT} \qquad (4)$$

[3] W. L. Bragg and E. J. Williams, Proc. Roy. Soc. **A145**, 699 (1934).
[4] C. Sykes and H. Evans, J. Inst. Metals **58**, 255 (1936).
[5] M. Volmer, *Kinetic der Phasenbildung* (Dresden, 1939).
[6] R. Becker, Ann. d. Physik **32**, 128 (1938).

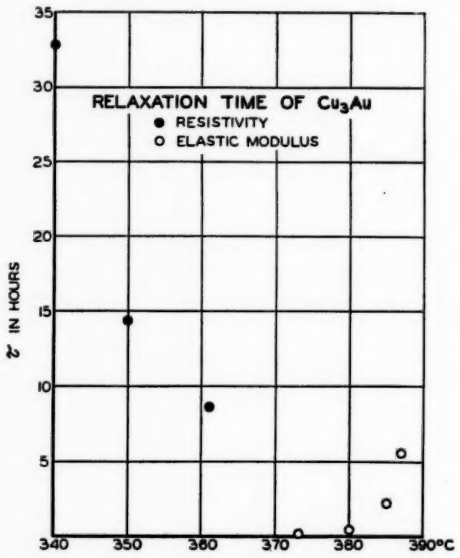

FIG. 8. The variation of τ with temperature for the disorder→order transformation, as determined from resistivity and elastic modulus measurements.

for the number N of nuclei formed per second per mole of solid solution. Here Q is the diffusion activation energy, and $A(T)$ is the energy of formation of a stable nucleus of the precipitating phase at the temperature T. If the rate of transformation of the alloy were primarily controlled by the rate of nucleation, then we could write

$$1/\tau = Ke^{-[Q+A(T)]/RT}. \tag{5}$$

Becker obtained the form of the function $A(T)$ by calculating the volume and surface free energies of the nucleus of the precipitating phase.

The analogous problem has not been carried through for the ordering process, but if a nucleation and growth mechanism is correct, we might make a guess as to the function $A(T)$. In general for such a mechanism, $A(T)$ will be some inverse function of the degree of undercool, and to a first approximation we will write

$$A(T) = \frac{L}{(T_c - T)/T}. \tag{6}$$

Qualitatively, this function

$$1/\tau = K_1 e^{-Q/RT} e^{-L/R(T_c - T)} \tag{7}$$

agrees with observation, for $1/\tau$ is zero at both $T=0$ and $T=T_c$, as is observed, and $1/\tau$ has a maximum at some intermediate temperature T_m, here found to be 370°.

By differentiating (7) above, we find the expression

$$L/Q = (T_c - T_m)^2/T_m^2. \tag{8}$$

Putting in the observed values $T_c = 386.8°$, $T_m \cong 370°$, and a value of $Q = 2.7 \times 10^4$ calories per mole[7] we obtain $L = 33$ calories per mole.

The physical significance of this energy L is not apparent. It must be concerned with the volume and surface energy difference between the ordered and disordered states, but a detailed calculation similar to Becker's would be required to discuss it in any greater detail.

[7] W. Jost, *Diffusion und Chemische Reaction in Festen Stoffen* (Dresden, 1937), p. 131; W. Jost, Zeits. f. physik. Chemie **B21**, 158 (1933).

Raman Spectrum of 1-Bromo-Dodecane

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(Received September 6, 1940)

Raman displacements, estimated intensities and depolarization factors have been measured for 1-bromo-dodecane in the liquid state. The strong, polarized frequencies 563 and 647, characteristic of the $-CH_2Br$ group, have the same constant values as do other members of the series from *n*-propyl to *n*-heptyl bromide inclusive. The weak, depolarized frequency 3009 is also probably associated with this group. Five of the observed frequencies agree rather well with values of infra-red active chain and end frequencies recently calculated by Whitcomb, Nielsen and Thomas for undecane, the mean deviation being 30 cm^{-1}. The intense, highly polarized frequencies 2850 and 2930 and the less intense, depolarized frequency 2961 appear in the bromide spectrum as well as in the spectra of many other compounds containing alkyl radicals.

INTRODUCTION

A SAMPLE of 1-bromo-dodecane, $C_{12}H_{25}Br$, became available[1] in connection with another investigation and since no Raman data had been reported for this compound, it seemed worth while to obtain displacements, estimated intensities and depolarization factors for it. Frequencies and estimated intensities have been reported by various workers[2] for all the normal alkyl bromides up to heptyl bromide, $C_7H_{15}Br$, but, with the exception of the methyl halides, depolarization factors seem to have been measured only for *n*-propyl chloride.[3]

EXPERIMENTAL

Details regarding the experimental methods have been given previously.[4] The spectrum was obtained with the 1-bromo-dodecane in the liquid state, at room temperature, with excitation by Hg 4358A. The liquid was carefully purified by distillation in a column and had a boiling point of 114–115°C at 3 mm and an index of refraction (n_D^{23}) of 1.4546.

[1] The authors are indebted to Dr. W. L. Wasley for this sample.

[2] For bibliography see K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt, Ergänzungsband*, p. 206.

[3] L. Simons, Soc. Scient. Fenn. Com. Phys. Math. **6**, No. 13 (1932).

[4] Forrest F. Cleveland and M. J. Murray, J. Chem. Phys. **7**, 396 (1939); M. J. Murray and Forrest F. Cleveland, J. Am. Chem. Soc. **61**, 3546 (1939).

RESULTS

The Raman displacements $\Delta\nu$ in cm^{-1}, the estimated intensities I, and the depolarization factors ρ are listed in columns one, two and three of Table I. Unusually broad lines are designated by the letter *b*. The lines 2884 and 2907 were not resolved on the depolarization spectrogram and the depolarization factor in this case is that measured for the unresolved doublet.

TABLE I. *Comparison of the Raman spectrum of 1-bromo-dodecane with calculated and observed infra-red frequencies for undecane.*

1-BROMO-DODECANE				UNDECANE*	
$\Delta\nu$	I	ρ	DESIGNATION	CAL.	OBS.
200	1*b*	—	δ	—	—
—	—	—	$\nu_8(\pi\sigma)$	385	—
563	7	0.4	ω(C-Br)	—	—
—	—	—	$\nu_6(o\sigma)$	604	—
647	6	0.6	ω(C-Br)	—	—
—	—	—	$\nu_4(o\sigma)$	907	907
1003	1	—	$\nu_5(o\sigma)$	1038	—
1076	3*b*	0.7	$\nu_8(\pi\sigma)$	1106	1066
1303	6	0.7	$\nu_9(o\pi)$	1354	1308
1441	9	0.8	δ(CH)	—	—
1457	3	0.8	$\nu_2(o\pi)$	1463	1463
—	—	—	$\nu_7(o\sigma)$	2273	—
—	—	—	$\nu_7(\pi\sigma)$	2320	2320
2724	1	0.7	$\nu_3(o\sigma)$	2752	—
—	—	—	$\nu_3(\pi\sigma)$	2778	2778
2850	10	0.2	$\omega_{11}(CH_2)$	—	—
2884	9	0.7	2δ(CH)	—	—
2907	5		$2\nu_2(o\pi)$	—	—
2930	7	0.1	$\omega_{11}(CH_3)$	—	—
2961	5	0.7	$\omega_\perp(CH_2)$	—	2944
3009	2	0.9	$\omega(CH_2Br)$	—	—

* Whitcomb, Nielsen and Thomas.

Discussion

Frequencies below 500 cm^{-1}

The 200 frequency is in the position to be expected if it is a deformation frequency involving the hydrocarbon chain. For example, Wood and Collins[5] report a frequency at 224 for the similar molecule, $C_{12}H_{25}OH$.

Frequencies characteristic of the $-CH_2Br$ group

It has been shown[6] that the C-Br valence vibration drops from 594 in CH_3Br to 557 in C_2H_5Br and then remains nearly constant for higher members of the series of normal alkyl bromides. In addition, a new frequency appears at 648 in the spectrum of *n*-propyl bromide and maintains approximately this value in higher members of the series. The behavior of the normal alkyl chlorides and iodides was quite similar.

The frequencies 563 and 647 observed in the present study are thus to be assigned to vibrations characteristic of the $-CH_2Br$ group, involving chiefly the C−Br bond. The appearance of *two* carbon-halogen frequencies for all except the first two members of the series is attributed by Kohlrausch[7] to the formation of two isomers by rotation of the $-CH_2X$ (X=halogen) group 180° about the adjacent C−C bond. He assigns the 557 frequency to the open form, the 648 frequency to the closed form.

The frequency 3009 is higher than usual for alkyl derivatives. Kohlrausch and Köppl[8] suggest that this frequency, which appears also for other members of the series, may be due to the $-CH_2Br$ group. The higher frequency is caused by the increase in the C−H force constant brought about by substitution of the bromine atom. For example, the C−H force constant in methyl bromide is 4.95×10^5 dynes/cm as compared with 4.81×10^5 dynes/cm in ethane.[9] This frequency is depolarized whereas the two near 600 were both somewhat polarized.

Chain frequencies

Recently Whitcomb, Nielsen and Thomas[10] have calculated the chain and end frequencies to be expected in the infra-red spectrum of undecane and have compared these calculated values with their observed values for the hydrocarbon in the gaseous state. Since Kohlrausch and his coworkers[6] have shown that the characteristic vibrations of the alkyl radical are almost uninfluenced by substitution of a halogen atom, it would be expected that some of the infra-red active vibrations of undecane would appear also in the spectrum of the 1-bromo-dodecane. To what extent this is the case may be determined by reference to Table I in which the calculated and observed values for undecane are listed in columns five and six, together with the designations of these frequencies in column four. Five of the frequencies observed for the bromide agree rather well with the values calculated for undecane, the average deviation being 30 cm^{-1}.

Symbols for other vibrations observed for the bromide (presumably weak or inactive in the infra-red) are included in column four, δ being used for deformation frequencies and ω for vibration frequencies. The strong, depolarized frequency 1441 is a δ(CH) frequency. The frequencies 2884 and 2907 may be the overtones 2δ(CH) and $2\nu_2(o\pi)$, respectively, with intensities augmented by resonance interaction with the Raman active fundamentals at 2850 and 2930. The highly polarized frequencies 2850 and 2930 and the depolarized frequency 2961 appear in a large number of compounds containing alkyl radicals and it has been suggested[11] that these frequencies may be identified with certain inner vibrations of the $-CH_3$ and $-CH_2-$ groups. These tentative assignments are indicated in Table I.

[5] R. W. Wood and G. Collins, Phys. Rev. **42**, 386 (1932).
[6] A. Dadieu, A. Pongratz and K. W. F. Kohlrausch, Akad. Wiss. Wien Ber. **141**, IIa, 480 (1932).
[7] K. W. F. Kohlrausch, Zeits. f. physik. Chemie **B18**, 61 (1932).
[8] K. W. F. Kohlrausch and F. Köppl, Zeits. f. physik. Chemie **B26**, 209 (1934).
[9] J. W. Linnett, J. Chem. Phys. **8**, 91 (1940).
[10] S. E. Whitcomb, H. H. Nielsen and L. H. Thomas, J. Chem. Phys. **8**, 143 (1940).
[11] Forrest F. Cleveland, M. J. Murray, Herschel H. Haney and Julia Shackelford, J. Chem. Phys. **8**, 153 (1940); Forrest F. Cleveland and M. J. Murray, J. Am. Chem. Soc., in press.

Efficiency of the Electrolytic Separation of Lithium Isotopes*

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(Received August 12, 1940)

The electrolytic separation coefficient, α, has been determined for the lithium isotope separation in the electrolysis of lithium chloride solutions at a mercury cathode. Its value was found to be $1.055 \pm$ about 0.005 and, within limits of error, was independent of temperature, of the fraction electrolyzed and of the amount of back reaction at the cathode. The factor was the same for LiCl dissolved in absolute ethyl alcohol as for aqueous LiCl. Isotopic analyses were made by a densimetric method of relative atomic weight determination. Crystalline materials with densities reproducible to the fifth decimal place were prepared. The observed separation is markedly larger than would be given by the exchange equilibrium. It is therefore certain that a kinetic mechanism is operative, although partial approach to equilibrium may enter as a secondary process. The data do not warrant a distinction between the various mechanisms which have been proposed as rate determining steps. They are consistent with Bell's quantum-mechanical explanation ($\alpha = 1.12$) or with a "diffusion layer" mechanism ($\alpha = 1.08$) if partial approach to equilibrium is assumed as a secondary step.

I. INTRODUCTION

THE discovery[1] that electrolysis is an effective means of separating isotopes of hydrogen proved of immense practical importance in the development of deuterium chemistry.[2] However, in spite of the extensive use which has been made of this process, and of a certain amount of experimental[3] and theoretical[4] effort to account for its effectiveness, the mechanism of isotope separation by electrolysis is still obscure.

Comparatively little attention has been given to the electrolytic separation of isotopes other than hydrogen. Washburn[5] made the discovery that oxygen isotopes were noticeably separated by electrolysis, and Johnston[6] found the electrolytic separation factor α[7] to be 1.008, for the electrolysis of alkaline solutions between iron electrodes. This compares with values in the neighborhood of 5 for hydrogen, and its very low value is in line with theoretical considerations advanced by Bell[8] on the basis of Gurney's theory of overvoltage.[9]

Eucken and Bratzler[10] were the first to investigate the electrolytic separation of lithium isotopes and were able to set 1.07 as an upper limit for α in the electrolysis of aqueous lithium sulfate at a mercury cathode. However, their method of analysis was accompanied by an experimental error about as large as the effect observed, so that no distinction could be made between this upper limit and an α of 1.00 (i.e., no separation). It was the purpose of the present investigation to determine α with higher accuracy, through an improved method of isotopic analysis, and to determine the possible influence of certain experimental factors.

During, and subsequent to, our own investigation experimental papers on the lithium separa-

* Presented before the Division of Physical and Inorganic Chemistry at the Detroit meeting of the American Chemical Society, September 10, 1940.

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[1] E. W. Washburn and H. C. Urey, Proc. Nat. Acad. **18**, 496 (1932).

[2] G. N. Lewis, J. Am. Chem. Soc. **55**, 1297 (1933); G. N. Lewis and R. T. MacDonald, J. Chem. Phys. **1**, 341 (1933).

[3] Appleby and Ogden, J. Chem. Soc. 163 (1936); R. P. Bell and H. Wolfenden, Nature **133**, 25 (1934); Collie, Nature **132**, 568 (1933); Eucken and Bratzler, Zeits. f. physik. Chemie **A174**, 273 (1935); A. Farkas, Trans. Faraday Soc. **33**, 552 (1937); Gunterschulze and Keller, Zeits. f. Elektrochemie **40**, 182 (1934); Horiuti and Okamoto, Sci. Papers Inst. Phys. Chem. Research (Tokyo) **28**, 231 (1936); Schwarz, Kuehler and Steiner, Zeits. f. Elektrochemie **40**, 298 (1934); Titani, Kuramo and Harada, Bull. Chem. Soc. Japan **9**, 269, 272 (1934); Topley and Eyring, J. Chem. Phys. **2**, 217 (1937); L. Tronstad, Zeits. f. Elektrochemie **40**, 556 (1934); Walton and Wolfenden, Trans. Faraday Soc. **34**, 436 (1938); Washburn, Smith and Frandsen, Bur. Stand. J. Research **11**, 453 (1933).

[4] R. P. Bell, J. Chem. Phys. **2**, 164 (1935); Bowden and Kenyon, Nature **135**, 105 (1935); Butler, Zeits. f. Elektrochemie **44**, 55 (1938); Eyring and Sherman, J. Chem. Phys. **1**, 345 (1933); Fowler, Proc. Roy. Soc. **A144**, 452 (1934); Halpern and Gross, J. Chem. Phys. **3**, 452 (1935); Horiuti and Polanyi, Nature **132**, 931 (1933); Topley and Eyring, J. Chem. Phys. **2**, 217 (1934).

[5] E. W. Washburn, E. R. Smith and F. A. Smith, Bur. Stand. J. Research **13**, 599 (1934).

[6] H. L. Johnston, J. Am. Chem. Soc. **57**, 484 (1935).

[7] For definition, cf. Urey and Teal, Rev. Mod. Phys. **7**, 34 (1935).

[8] R. P. Bell, J. Chem. Phys. **2**, 164 (1934).

[9] Gurney, Proc. Roy. Soc. (London) **A134**, 137 (1932).

[10] A. Eucken and Bratzler, Zeits. f. physik. Chemie **A174**, 269 (1935).

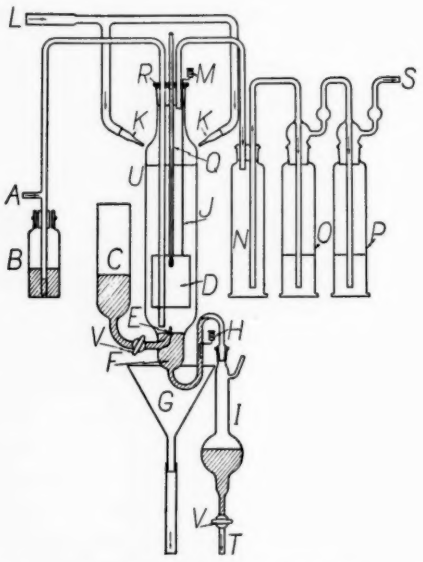

FIG. 1. Apparatus for electrolysis. *A*—Hydrogen inlet, *B*—mercury pressure release, *C*—Mercury reservoir, *D*—platinum anode, *E*—jet from which Hg falls on the cathode surface, *F*—mercury cathode, *G*—funnel for carrying away cooling water, *H*—cathode terminal, *I*—amalgam reservoir, *J*—platinum anode lead, *K*—jets for cooling water supply, *L*—cooling water inlet, *M*—anode terminal, *N*—trap, *O*—washing bottle containing acetone, *P*—washing bottle containing water, *Q*—thermometer, *R*—paraffin, sealing in the top of the apparatus, *S*—hydrogen outlet, *T*—amalgam outlet, *U*—glass cell, heavily coated with paraffin, containing solution of lithium chloride, *V*—stopcock.

tion were published by Taylor and Urey[11] and by Holleck.[12] Taylor and Urey electrolyzed aqueous lithium hydroxide at a mercury cathode and obtained an α of 1.020 on the basis of a mass-spectrometer analysis by Brewer, while Holleck electrolyzed a solution of 9 kg of LiCl, in three steps, and obtained $\alpha=1.079$ by a chemical atomic weight method of analysis. Our own value is intermediate between these ($\alpha=1.055$) and is found to be practically independent of the experimental conditions of electrolysis.

II. Experimental Apparatus and Method of Analysis

A. The electrolysis

The electrolyses were carried out in an apparatus similar to that used by Eucken and Bratzler,[10] and shown in cross section in Fig. 1.

[11] T. I. Taylor and H. C. Urey, J. Chem. Phys. **5**, 597 (1937).
[12] Holleck, Zeits. f. Elektrochemie **44**, 111 (1938).

The cell was of Pyrex, heavily coated on the inside with "biolloid" paraffin. It was closed at the top with a paraffined rubber stopper through which passed the platinum lead to the anode, and paraffined glass tubes and thermometer. The anode was of platinum and the cathode was a flowing mercury electrode. The mercury was supplied from the reservoir *C* and its rate of flow regulated at speeds between about 4 and about 10 liters per hour. The electrolyte was an aqueous solution of pure lithium chloride and was constantly stirred, during electrolysis, by a stream of hydrogen admitted through the paraffined tube *A*. The chlorine gas carried out with the hydrogen stream was absorbed in acetone in the wash bottles *O* and *P*. Electrical contact with the cathode was made through the sealed-in tungsten lead at *H*. The temperature of the electrolyte was regulated by means of streams of water which flowed over the cell from jets near the top (*K*, *K*) and were carried off by the funnel *G*.

The mercury used for the flowing cathode was redistilled under vacuum, washed with dilute nitric acid and then with distilled water. The washings were repeated before every run.

The amalgam formed in each electrolysis was placed in heavily paraffined earthenware jars and allowed to react with distilled water in the presence of platinum foil as a catalyst. A portion of the lithium hydroxide solution so formed was removed for the isotopic analysis. This portion of lithium hydroxide was first converted to the carbonate by precipitation with CO_2 and, eventually, to lithium fluoride, as subsequently outlined.

B. The analysis

(*a*) *Method.*—In previous isotopic work with lithium analyses have been made by the mass spectrometer[11] or by chemical atomic weight methods.[10,12] The first requires relatively costly apparatus and the second necessitates successive electrolyses on an initially large quantity of starting material. In this work we have developed the inexpensive "crystal flotation" method, of Lewis and MacDonald,[13] into one of high precision. By its use the electrolytic separation

[13] G. N. Lewis and R. T. MacDonald, J. Am. Chem. Soc. **58**, 2519 (1936).

factor can be measured with good accuracy in a single-step electrolysis of a comparatively small quantity of starting material.

The method is essentially the "free submerged float" method[2] employed extensively for the isotopic analysis of water. Changes in the isotope abundance ratio are determined from changes in density of crystalline material into which the element undergoing analysis is converted. Changes in the crystal density are determined with high precision by observation of the narrow temperature limits that distinguish rise and fall of the individual crystals submerged in a suitable flotation liquid whose density-temperature coefficient is determined in a previous calibration. A "standard" crystal, of normal isotopic composition, serves as a reference standard and corrects for slow changes in the composition (and density) of the flotation liquid. For isotopic analyses only the density-temperature coefficient of the liquid need be known accurately.

We have found that, for lithium analysis, purified crystals of lithium fluoride in a flotation medium of bromoform admixed with small amounts of *n*-pentanol and *n*-hexanol form a sensitive and satisfactory analytical system. These alcohols were used to act as negative catalysts of decomposition of the bromoform by air and light, in place of the more usual ethanol,[14]

TABLE I. *Sample flotation runs on three crystals of normal* LiF.

1	2*	3**
3.300*F*	3.300*F*	3.290*R*
3.294*R*	3.290*R*	3.303*F*
3.300*F*	3.299*F*	3.293*R*
3.295*R*	3.292*R*	3.297*F*
3.299*F*	3.300*F*	3.295*R*
3.295*R*	3.294*R*	3.303*F*
3.300*F*	3.296*F*	3.294*R*
3.296*R*	3.299*F*	3.300*F*
	3.295*R*	3.294*R*
	3.297*F*	3.299*F*
	3.295*R*	3.295*R*
		3.299*F*
F. T.	F. T.	F. T.
3.298±0.002	3.296±0.002	3.297±0.002

* Grown at same time as 1.
** Grown at another time but from same material as 1 and 2.

[14] Experiments in which oxygen was bubbled through various alcohol bromoform mixtures, with exposure to sunlight, showed that the higher alcohols are more effective negative catalysts than ethanol.

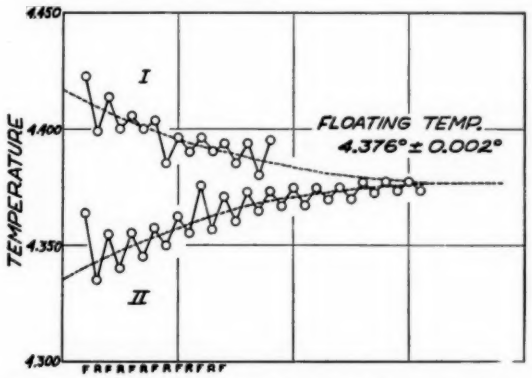

FIG. 2. Plot of successive rising and falling temperatures for a crystal of LiF when the thermostat was held above (I) or below (II) the flotation temperature for some time, before measurements were begun.

because of their approximately equal volatility to that of bromoform.

Flotations were carried out in a glass-stoppered tube immersed in a small water bath, whose temperature was manually controlled to within 0.001°C. The crystal was illuminated through small windows in the walls of the water bath and was observed against the cross-hairs of a telescope. Temperatures were read on a calibrated Beckmann thermometer.

The floating temperatures were determined in the following manner. The temperature of the water bath was alternately raised and lowered to get rising (R) and falling (F) temperatures of the crystal. The temperature interval between R and F was gradually narrowed until the *same* interval of 0.004° to 0.005° could be passed over four times with four reversals of motion. The temperature, T, at the midpoint of this interval was then taken as the flotation temperature ±0.002°. In Table I are some flotation records on three crystals of recrystallized ordinary LiF, made as a preliminary test of the method. These serve to illustrate the sensitivity and reproducibility obtained.

We experienced some difficulty, in a few early runs, from rapid drift in the apparent temperature of flotation. This was observed when the approach to equilibrium was begun with the water bath initially several tenths of a degree away from the correct flotation temperature and is probably ascribable to convection currents in the flotation liquid that may result from rapid variations in the temperature of the bath. This

is illustrated in Fig. 2 for a crystal for which the bath was purposely held, first, at a temperature a few tenths of a degree above the crystal flotation temperature before flotation bracketing was begun (curve I) and, secondly, at a temperature somewhat below the flotation temperature before measurements were taken (curve II). When the bath was held for several minutes prior to measurements at a temperature within a few hundredths of a degree of that of flotation this difficulty was not encountered. A rough estimate of flotation temperatures in advance of the measurements thus made it possible to eliminate the annoyance illustrated in the graph, for most of the later analyses.

(*b*) *Preparation and calibration of the bromoform mixture.*—A suitable composition for the flotation liquid was found to be: bromoform, 115.7 g; *n*-hexanol, 170 drops (68 drops equal 1 ml); *n*-pentanol, 149 drops. This liquid was prepared in the following manner. Merck's bromoform (4 percent ethanol) was washed several times with water, dried with calcium chloride, and vacuum distilled. The middle portion of the distillate was collected in a weighed receiver that contained initially a small quantity of the pentanol-hexanol mixture. After distillation further amounts of pentanol and of hexanol were added to bring the mixture to the desired composition. The mixture described was found to remain practically constant in density over several days use, and was easily corrected for small density changes by frequent checks against the flotation temperatures of "standard" crystals. Discoloration of this liquid, in sunlight, was gradual and no appreciable solubility of lithium fluoride in the mixture was detected by the method of evaporating a portion of the liquid on a watch glass after it had been in use for twelve or more crystal flotations.

The density-temperature coefficient of the liquid, in the neighborhood of 27°C, was determined by hydrostatic weighings. A Pyrex glass bob 9 ml in volume, partially filled with mercury, was suspended from a balance pan by a platinum wire 0.004″ in diameter and weighed successively in air, in water, and in the bromoform mixture at various temperatures. The necessary corrections for buoyancy in air (applied to the brass weights in all weighings and to the Pyrex bob

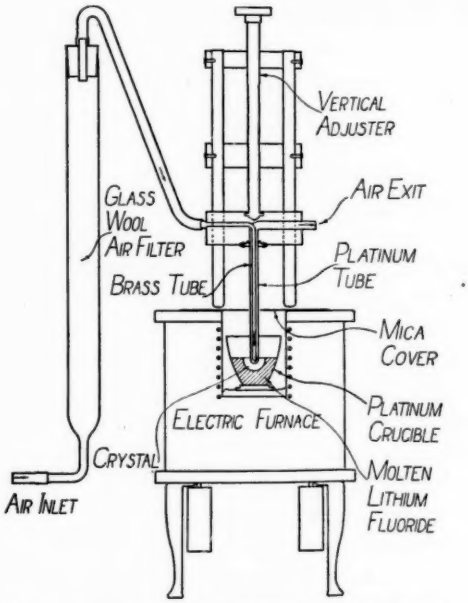

FIG. 3. Apparatus for growing crystals of LiF.

for the weighing in air) and for the thermal expansion of Pyrex[15] were applied. Individual densities were reproducible to within about ± 0.00005 g/ml and 17 points over a 3° range in temperature gave a good straight line with a slope of $-2.49(\pm 0.01)\times 10^{-3}$ g/ml/degree. 0.001°C in the crystal flotation temperature thus corresponds to 2.49×10^{-6} g/ml in the density of LiF and, if the thermal coefficient of expansion of LiF were zero, to 2.45×10^{-5} atomic weight units of lithium and to 2.45×10^{-3} percent in the isotopic composition of lithium. A correction of 0.26×10^{-3} for the temperature coefficient of the density of LiF [16] reduces these latter figures to 2.19×10^{-5} atomic weight unit of lithium and to 2.19×10^{-3} in the atomic percent of the lighter isotope in the lithium. Determination of flotation temperatures of pure crystals to $\pm 0.002°$ thus corresponds to an isotopic analysis to within about 0.004 percent of Li^6.

The calibration was made directly to the scale of the Beckmann thermometer employed in the crystal analyses. A precision thermometer, graduated in intervals of 0.02° and calibrated by the

[15] Buffington, J. Am. Chem. Soc. **48**, 2305 (1926).

[16] This is based on a graphical extrapolation of the data of Adenstedt [Ann. d. Physik **26**, 69 (1936)] who measured the linear β's for LiF at several temperatures between that of liquid air and 0°C. Extrapolation to 27°C yields 33.5×10^{-6} for β; 100×10^{-6} for the volume coefficient; and 0.264×10^{-3} for the density coefficient, per degree C.

National Bureau of Standards was used only in the water weighings at 27.612°C to obtain the correct volume of the bob. We employed the tables given in the *International Critical Tables*[17] for the density of water at this temperature. Actually, the precise value of the bob volume was of secondary importance to us since, by our method of calibration, and of use, only the temperature coefficient of the liquid density is needed. Comparison with the flotation temperature of "standard" crystals eliminates both the need for correct absolute densities or temperatures and the difficulties that would otherwise arise from slight contamination of the liquid or slight variation in its composition subsequent to calibration.

(*c*) *Preparation of crystals for the analysis.*—As the result of considerable preliminary investigation we adopted a scheme of purification and crystallization which has as its main processes: double recrystallization of Li_2CO_3 from hot aqueous solution; precipitation of LiF in ammoniacal solution and eventual crystallization from fused LiF by a method similar to that employed, for other salts, by Kyropolous.[18] The entire procedure consisted of the following steps:

(1) 5 to 8 grams of Li_2CO_3 prepared from the portion of aqueous LiOH held back for the analysis (p. 870)[19] were dissolved in 1.5 liters of conductivity water and twice recrystallized by boiling down the solution to 25 ml. The residual mother liquor was separated from the crystals by decantation. These recrystallizations were carried out in a crystallizing dish of pure silver.

(2) The recrystallized Li_2CO_3 was dissolved in pure aqueous HCl, NH_4OH was added until the solution was alkaline and the solution filtered.

(3) LiF was precipitated by the addition of a slight excess of NH_4F. The precipitate was filtered and washed.

(In all of the above steps glass vessels and accessories were heavily coated with biolloid paraffin.)

(4) The LiF was fused in a platinum crucible heated by an electric furnace; the melt heated to a temperature about 100° above the melting point of LiF; and crystallization produced about the tip of a closed platinum tube inserted into the melt. The apparatus for this step is diagrammed in Fig. 3. To produce crystallization the tip of the 6-mm OD platinum tube was lowered a short distance into the melt by means of the adjusting screw and the temperature of the furnace lowered slowly while a slow stream of air was passed through the tube. When the crystal that formed reached a convenient size it was withdrawn from the melt and held a short distance above the surface of the LiF in the crucible while the furnace was slowly cooled, over a period of several hours, to room temperature. A slight discoloration of the platinum crucible occurred at the surface of the melt but no discoloration appeared on the platinum tube, and spectroscopic examination of LiF from a melt showed no trace of platinum.

(5) Selected fragments of the crystal which formed around the tip of the platinum tube were annealed at a temperature 50° below the melting point of LiF; cooled slowly to room temperature; and were ready for flotation. The fragmentation was the result of strains that were set up as the hemispherical crystal cooled on the platinum tube. The fault lines were radial, the breaks sharp and the segments clear. For our purpose this fragmentation was not troublesome since small crystals are adequate for flotation. Fragments were examined under a magnifying glass and any which showed surface irregularities, or cracks, were discarded.

Tables I and II show the character of the agreement obtained between crystal fragments of

TABLE II. *Relative flotation temperatures on 10 crystals from three different preparations of normal* LiF.

PREPARATION	CRYSTAL	FLOATING TEMPERATURE
1.	*A**	0.000±0.002
	B	0.015±0.002
	*C**	0.000±0.002
	*D**	0.000±0.002
2.	*A*	−0.017±0.002
	B	0.037±0.002
	C	0.011±0.002
	*D**	0.000±0.002
	*E**	−0.001±0.002
3.	*A**	−0.003±0.002

* High density, agreeing results attributed to normal crystals.

[17] Int. Crit. Tab. Vol. 3, p. 25.

[18] Kyropolous, Zeits. f. anorg. Chemie **154**, 308 (1926).

[19] In the preparation of "standard" crystals we started directly with recrystallization of Baker and Adamson's reagent quality Li_2CO_3. Li_2CO_3 from the same reagent bottle, dissolved in the proper equivalent of aqueous HCl, served as the starting material in the electrolyses.

TABLE III. *Electrolysis I—stepwise electrolysis of aqueous* LiCl.

STEP	1	2	3	4
Average temperature of electrolyte (0°C)	40	30	35	40
Average current density (amp./cm²)	0.5	0.57	0.63	0.47
Weight of lithium in starting material (g)	64.820	12.222	7.722	3.762
Weight of lithium found in amalgam	13.229	9.071	5.190	1.553
Fraction of lithium in the amalgam (F)	0.2041	0.742	0.672	0.413
Current efficiency	0.36	0.63	0.65	0.60
Weight of lithium (from the amalgam) purified for analysis	1.007	1.349	1.428	1.553
Flotation temperatures of different crystal fragments, relative to standard crystals†	*0.170	*0.269	*0.356	*0.477
	H	*0.269	*0.327	0.501
		*0.269	*0.355	0.679
			*0.361	*0.477
				*0.475
				*0.465
				H,H,H
Temperature adopted	0.170	0.269	0.357	0.474
Percent Li^6 (normal lithium taken as 7.811% Li^6)	8.181	8.398	8.589	8.844
α (cumulative)	1.058	1.059	1.056	1.052

† The crystals marked with asterisks were taken to be physically undeformed and free from contamination. *H*'s represent additional fragments found, in preliminary flotation, to be of such low apparent density that they could not be included as undeformed crystals. Hence their accurate flotations were not determined. Reference to them is included here to indicate the typical results to be expected from a group of crystal fragments.

the same crystalline preparation and between different crystallizations of the same isotopic material. These data were obtained on LiF crystals prepared from Li_2CO_3 with normal isotope composition, and the floating temperatures are all taken relative to crystal fragment 1*A*. The results are typical in that they show agreement among about half of the selected crystal fragments (those marked with asterisks) to within the accuracy of flotation measurements while practically all of the remainder float at widely diverse *higher* temperatures corresponding to abnormally low densities.[20] The latter, diverse results are attributed to undetected cracks, or other inhomogeneities in the crystal fragments. Only those crystals, marked with an asterisk, which agree with each other and are of relatively high density, are regarded as significant for purpose of analysis.

III. EXPERIMENTAL RESULTS OF ELECTROLYSES IN AQUEOUS LiCl SOLUTION

An initial electrolysis was carried out in four steps, to obtain a relatively large change in isotopic composition. The bulk of the lithium found in the amalgam from the first step was reconverted to LiCl to form electrolyte for the second step. This procedure was repeated for the third and fourth steps. The data from this fractional electrolysis are given in Table III.

The fraction electrolyzed, *F*, was determined by electrometric titration of the resulting LiOH (corrected for the amount of sample held out for isotopic analysis). Aqueous HCl, standardized against Na_2CO_3, was used as the titering agent with a platinum-tungsten bimetallic electrode as indicator.

By the current efficiency is meant the ratio of the number of gram atoms of lithium in the amalgam to the number of faradays of electricity used in the electrolysis. Departure of this ratio from unity is attributed to back reaction with water at the amalgam surface. The amount of back reaction could be reduced by increasing the flow of mercury. This was done in steps 2, 3 and 4 for which the rate of mercury flow was about double that employed in step 1.

The separation factor was checked at each step with samples removed for analysis. The factor for the first step was computed from the formula

$$(\alpha-1)\log(1-F)=\log(Li^7/Li^6)_i - \log(Li^7/Li^6)_r, \quad (1)$$

in which the subscripts refer to the isotope ratios in initial electrolyte and in the residual electro-

[20] Values lower than normal, such as for crystal 2A, are less common and are probably due to inadvertent contamination, most likely with sodium. We found in preliminary experiments that sodium contamination would increase the density of crystals while contamination with alkaline earths would reduce it. Our method of purification, however, is very effective in eliminating the influence of initial sodium contamination. Thus, initial contamination with 10 percent Na_2CO_3 yielded crystals, from the regular process of purification, that were only 0.030° low in flotation temperature. It should be remarked that the Ca contamination is much more difficult to eliminate.

lyte, respectively. The latter ratio was computed from the increase in Li^6 content observed for the amalgam lithium and from the proportionate amounts of lithium in the residue and in the amalgam. The isotope ratio in normal Li was taken to be 11.804. As our method of analysis is itself a relative one our values of α are not sensitive to the choice of the normal ratio. F in Eq. (1) is the fraction electrolyzed, referred to in a preceding paragraph.

The same formula is applicable separately to the later steps, with (Li^7/Li^6) set equal to the analysis found (or computed) for the amalgam lithium in the next preceding step. The values of α recorded in the table are cumulative ones—i.e., the values obtained when it is assumed that α remains constant during the successive steps of fractional electrolysis. They were obtained by computing Li^6 concentrations in the amalgams from the various steps, by successive use of Eq. (1), with various choices of α and comparing the computations with the observed Li^6 analyses.

Variations in the temperature of the tap water between days on which these steps were run made it impracticable to run them at a common temperature. Although the agreement is reasonably good between values of α computed from analyses at the several steps it was felt that there might be some significance of temperature in the general trend of α through the last three steps. Although this interpretation is not consistent with the (less accurate) value from the first step a further series of (single step) electrolyses was carried out as a further test of possible significant influence of temperature and of the amount of back reaction.

The data from these electrolyses are shown in Table IV. They do not indicate any significant dependence on either the temperature or the amount of back reaction. From the latter we may conclude that there is little difference in the reactivity of the lithium isotopes toward water, at an amalgam surface.

The mean of the eight values for α is 1.055 with only one value lying outside of the limits ± 0.005. The small error in the reproducibility of crystal densities ($\pm 0.002°$ each on standard sample and on specimen) alone imposes a lack of reproducibility of about ± 0.002 on α. Variations of ± 0.005 cannot be regarded as significant in view of other sources of reasonable experimental error.

Discussion of Results. Electrolysis of LiCl Dissolved in Absolute Alcohol

Our value of 1.055, with temperatures between 25° and 40° and current densities between 0.5 and 0.7 amp./cm² is to be compared with Holleck's[12] value of 1.079, at 38–40° and a current density of 0.06–0.08 amp./cm², with Taylor and Urey's[11] 1.020, at 25° and 0.62 amp./cm²; and with a more recent value of 1.039, reported by the same authors[21] for electrolysis of aqueous LiCl at 36° and 0.62 amp./cm². Kendall[22] reported that the separation of mercury isotopes was more efficient at low than at high current densities. It is possible that similar behavior for lithium may account for

[21] T. I. Taylor and H. C. Urey, J. Chem. Phys. **6**, 429 (1938). Our preliminary value of 1.062 referred to in this paper was based on data which had not been corrected for the thermal expansion of LiF.

[22] Kendall, J. Am. Chem. Soc. **55**, 2612 (1933).

Table IV. *Single step electrolyses of aqueous* LiCl.

Electrolysis	II	III	IV	V
Temperature of electrolyte (°C)	35	35	35	25
Current density	0.71	0.71	0.71	0.71
Weight of lithium in starting material (g)	40.583	7.580	23.925	15.195
Weight of lithium in amalgam (g)	3.773	3.308	3.066	2.762
Fraction of lithium in amalgam	0.0930	0.4364	0.1282	0.1818
Current efficiency	0.58	0.47	0.25	0.36
Flotation temperatures of different crystal fragments, relative to standard crystals*	*0.192	*0.115	0.238	*0.166
	*0.189	*0.116	*0.165	*0.171
	*0.188	*0.116	*0.161	*0.175
	H,H	*H,H*		*0.173
Temperature adopted	0.190	0.116	0.163	0.171
Percent Li^6 (normal lithium taken as 7.811% Li^6)	8.225	8.064	8.167	8.184
α	1.060	1.048	1.052	1.057

* See footnote to Table III.

the difference between Holleck's value of α and our own but we have no data to confirm this. In the small range of 0.47 to 0.71 amp./cm^2 there was no significant dependence on current density. Obviously, current density cannot explain the difference between our own results and those of Taylor and Urey nor between their own sets of data with LiOH and LiCl, respectively. Temperature appears likewise not to be an important factor. At first glance it might appear that a difference between electrolyses in LiOH and LiCl could arise from the nature of the anion in the electrolyte (Holleck's work, and our own, were done with LiCl. Taylor and Urey's second electrolyses were for the purpose of clarifying the difference between these and their own earlier value with LiOH). However, it is apparent that LiOH must have formed in considerable concentrations in our own cell, and in those of Holleck, due to the considerable amounts of back reaction. Our own electrolyses must therefore have had a good deal of the characteristics of LiOH electrolyses. If the character of the anion were an important factor we would expect a correlation with the amount of back reaction and with the fraction electrolyzed. That correlation does not exist. Taylor and Urey[21] suggest that differences in the strength of the electrolyte may be responsible for the disagreement of our results and those of Holleck with their own LiCl data. But this clearly would not account for the difference between their own data for LiOH and for LiCl; nor does it seem probable, in view of the close agreement we obtain for electrolyses in ethyl alcohol with those in water (cf. *seq.*). Neither does the suggestion agree with the results in other isotopic separations.[23]

Efforts to explain[4] the electrolytic separation of isotopes have involved two kinds of factors: (1), kinetic factors (relatively large) determined by the processes leading to different *rates* of electrolysis of the different isotopic species—and (2), an equilibrium factor due to the fact that the electrolyzed material must remain in contact with residual electrolyte, for a certain length of time, under conditions which lead to isotopic exchange between the media.

[23] H. L. Johnston and C. O. Davis. To be published in J. Am. Chem. Soc.

Lewis and MacDonald[13] found the equilibrium factor for the exchange between isotopes in lithium amalgam and in LiCl dissolved in absolute C_2H_5OH to be 1.025 (possibly a lower limit). This figure corresponds closely to the exchange factor for equilibrium between lithium and lithium hydride computed on theoretical grounds by Urey and Greiff.[24] On the assumption that this is also the correct factor for isotopic exchange between lithium amalgam and aqueous lithium hydroxide, Taylor and Urey conclude, from their value of 1.020 for the electrolytic α in LiOH solution, that the equilibrium factor probably accounts for the whole of the separation obtained in the electrolysis. In our own results and in those of Holleck a kinetic factor must have been operative to a considerable extent. It would appear that the same conclusion would have to be drawn by Taylor and Urey for their results with LiCl.[25]

To make the comparison with the equilibrium factor of Lewis and MacDonald more direct we have carried out an electrolysis with an electrolyte consisting of LiCl dissolved in pure ethyl alcohol. The moisture-free LiCl used as solute was obtained by dissolving Li_2CO_3 in 12*N* HCl and evaporating the solution to dryness in an atmosphere of dry hydrogen chloride. The results of this electrolysis are shown in Table V. Within limits of error this value of α is identical with that found for electrolysis of aqueous lithium chloride. This indicates that a kinetic mechanism

TABLE V. *Electrolysis of* LiCl *dissolved in absolute* C_2H_5OH.

Temperature	42°C
Current density	0.21 amp./cm^2
Weight of lithium in starting material	15.069 g
Weight of lithium in amalgam	1.507 g
Fraction electrolyzed	0.1010
Flotation temperatures relative to standard crystals*	* 0.169
	0.192
	0.186
	* 0.166
	H,H
Temperature adopted	0.168
Percent Li	8.178
α	1.053

* See footnote to Table III.

[24] Urey and Greiff, J. Am. Chem. Soc. **57**, 321 (1935).

[25] Unless the correct equilibrium α is really higher than 1.025. Lewis and MacDonald take 1.025 as a lower limit, and the comparison with LiH is indirect.

is operative in the separation and implies that the same mechanism is operative in alcoholic as in aqueous solution. However, there may be partial approach to equilibrium as a secondary process. For this reason, the observed α may be lower than the kinetic value corresponding to any particular mechanism.

Our data do not appear to warrant a distinction between the several explanations which have been proposed[4] to account for the kinetic factor of electrolytic separation processes. In general, several distinct steps in an electrolytic process are recognized at which isotopes may exhibit appreciable differences in rate. The difficult part is to identify the rate-determining step. Bell's[8] effort to calculate α for lithium isotopes, by quantum-mechanical methods, is based on the supposition that the rate limiting step is the penetration of solvent sheath surrounding the hydrated lithium ion, by an electron. In his calculation Bell used an improbable value for the heat of hydration of Li^+. Repeating this calculation with the more reasonable value of 140 kcal., computed by Gurney[26] and taking 5 to be the best average α for hydrogen we obtain for Li, $\alpha=1.12$. If Bell has chosen the correct rate determining step then the α obtained in this research represents a slightly better than 50 percent approach to equilibrium. Data are not available to apply Bell's theory to the alcohol electrolysis.

However the results are also consistent with other choice of the rate determining step. For example, ionic diffusion and migration through a "diffusion layer" are known to play the rate determining role in some electrolyses,[27] including that of the halogens. The ionic current, in electrolyses for which this is the current-determining step, is given by

$$i=(1-C_e/C_0)kn_AFC_0/\delta t_B \qquad (2)$$

where k is the diffusion coefficient of the cation; n_A its valence; F, the faraday; δ, the thickness of the diffusion layer; t_B the transference number of the anion and C_0 and C_e the concentrations of cation in the body of electrolyte and at electrode surface, respectively. For isotopes this would reduce to

$$i_x/i_y=\left[\left(1-\frac{C_e}{C_0}\right)_x k_x \Big/ \left(1-\frac{C_e}{C_0}\right)_y k_y\right](C_{0x}/C_{0y})$$

and would become, at limiting current,

$$(i_x/i_y)(C_{0y}/C_{0x})=k_x/k_y=(M_x/M_y)^{\frac{1}{2}} \qquad (3)$$

where the M's represent ionic masses. For lithium isotopes this would give a kinetic separation factor of 1.08. The same factor would be applicable in alcoholic as in aqueous solution, providing diffusion were the rate determining step in each.

Neither the exchange α (1.025), the quantum-mechanical α (1.12) or the diffusion α (1.08) would possess sensible temperature dependence and such differences in temperature coefficient as are predicted lie within the error limits of our data. The same would be true for other possible rate-determining steps.[4] If, however, the observed α represents partial approach to equilibrium from an initial kinetic separation, it is to be expected that temperature might play a larger part, by bringing about a change in the extent to which equilibrium is approached. If such an effect exists between 25° and 40°, under the conditions of our electrolyses, it is below 0.01 unit in α.

Crystal Density

It is recognized that even physically well-formed crystals may contain discontinuities in their lattices with resulting minute cracks and mosaic structure. However, the present results indicate that crystalline LiF of macroscopic dimensions may agree in density to at least the fifth decimal place.

The crystal density determinations described here were relative measurements. A determination of the absolute density of crystals of normal lithium fluoride (to be described elsewhere) yielded 2.63835 ± 0.00007 for $d_{27.67°C}$ relative to water at 4°C. Using Adenstedt's[16] data for the thermal expansion of LiF at 27° this reduces to $d_{25°}=2.63905\pm0.00007$.

[26] Gurney, *Ions in Solution* (Cambridge University Press, 1936), p. 202.
[27] J. N. Agar and F. P. Bowden, Proc. Roy. Soc. **A169**, 206 (1938).

Verification of the Theoretical Numbers of Components into Which Electronic Energy Levels Are Decomposed by Crystal Fields

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A GIVEN electronic energy level of an ion in an electrostatic field is decomposed, according to theory, into a number of sublevels which depend on the symmetry of the field. The number of these component levels has been derived by general methods in a well-known paper of Bethe[1] for levels of different quantum character and for fields of various crystallographic symmetries.

It has been supposed that such a description would apply to the ions of the rare earths in crystals and that the symmetry of the field is to be identified with the symmetry of the environment about the ions in the lattice. The facts are that the spectra of these ions consist of rather isolated groups of lines and the lines within the groups vary in number when the ions are present in crystals of different symmetries. Further qualitative confirmation comes from the usual appearance of more lines within the groups when the crystals are of lower symmetry.

The number of lines in the spectra are, of course, also governed by selection rules. Because of the high concentration of matter in crystals and the variety of interaction there, the selection rules for independent systems take on an approximate character.[2] Hence, we should not be unprepared for transitions between almost all combinations of the sublevels. In this connection, it may be mentioned that Gobrecht[3] obtained transitions between terms within the basic multiplet.

Only a few structures of crystals of the rare earths have been unambiguously determined. Of these we shall discuss the anhydrous fluorides RF_3. They are hexagonal $D_{6h}{}^3$ and the symmetry of matter about the rare earth ion R^{+++} is C_{2v}.[4] To obtain a more symmetrical environment, we investigated whether mixed crystals of a rare earth fluoride and a large preponderance of bismuth fluoride could be prepared in the belief that they would maintain the symmetries of pure bismuth fluoride BiF_3. The latter is cubic $O_h{}^5$ and the bismuth ions are at the center of cubic holohedral symmetry O_h.[5] Bismuth, it is well known, forms salts which are isomorphic with the corresponding salts of the rare earths. It has, in fact, turned out that the fluorides are miscible and assume the cubic structure appearing as isotropic in the polarizing microscope.

For spectroscopic purposes we have chosen europium, both in the pure and in the mixed fluorides.[6] The crystal field about Eu^{+++} has then the symmetry C_{2v} in the former and O_h in the latter.

There are three prominent groups of lines in the visible absorption spectrum of europium ions in crystals—in the yellow at about 5780A, in the green at 5250A, and in the blue at 4650A. Study of the fluorescence of salts of europium led Gobrecht[7] to ascribe these groups to the transitions: from $J=0$ to $J=0$ for the yellow; from $J=0$ to $J=2$ for the group in the green, and from $J=0$ to $J=3$ for the blue. We have obtained confirmation of these assignments in studies of the Zeeman effects of some crystals and also consistent with these assignments are the spectra from many crystals and solutions.

A crystal field having a symmetry C_{2v}

[1] H. A. Bethe, Ann. d. Physik **3**, 133 (1929).
[2] It has become fairly certain that the selection rules for quadrupole and magnetic dipole radiation are applicable in many of the transitions. See J. H. Van Vleck, J. Phys. Chem. **41**, 67 (1937).
[3] H. Gobrecht, Physik Zeits. **37**, 549 (1936).
[4] I. Oftedal, Zeits. f. physik. Chemie **B13**, 190 (1931); *Strukturbericht* [II] (Akademische Verlagsgesellschaft, Leipzig, 1937), pp. 27, 288.
[5] O. Hassel, S. Nilssen, Zeits. f. anorg. allgem. Chemie **181**, 172 (1929). *Strukturbericht* [II] pp. 22, 290.
[6] Anhydrous europium fluoride was prepared by adding 40 percent hydrofluoric acid to a hot, saturated aqueous solution of europium nitrate. The precipitate was washed thoroughly and dried in a vacuum at 180°C.
The mixed bismuth-europium fluoride was prepared in the same way as pure bismuth fluoride (Method I in *Strukturbericht* II p. 290), except that 10 mole percent of europium nitrate was added to the bismuth nitrate in solution before the precipitation. The crystals were fused in ammonium acid fluoride (ammonium fluoride was also employed in another fusion, with identical results). The heating was continued until no more fumes were evolved and in the process the temperatures was raised to about 800°C.
[7] H. Gobrecht, Ann. der Physik **28**, 670 (1937).

would theoretically lift all the degeneracy of the "unperturbed" levels. $J=0$ would remain single; $J=2$ would be split into five components, and $J=3$ into seven. Pure europium fluoride EuF_3 actually exhibits the maximum number of lines in the spectrum, i.e., it reveals all the levels. The group in the yellow is single 5780A; in the green there are five lines—5252.3A, 5247.5A, 5245.6A, 5244.1A, 5241.3A; and in the blue seven—4649.1A, 4648.4A, 4646.1A, 4644.7A, 4642.7A, 4640.6A, 4638.1A.

A crystal field having the symmetry O_h would lift the degeneracy partially. According to theory, $J=0$ would remain single; $J=2$ would decompose into two sublevels, and $J=3$ into three. The spectrum of the cubic mixed fluoride Bi-Eu F_3 conforms precisely to these numbers. There is but one line in the yellow 5780A; the group in the green consists of two lines 5259.1A, 5248.0A; and the group in the blue consists of three 4656.6A, 4647.5A, 4638.0A.

We are much indebted to the Penrose Fund of the American Philosophical Society for the support it has given this investigation.

NOVEMBER, 1940 JOURNAL OF CHEMICAL PHYSICS VOLUME 8

The Local Field in Polarized Dielectrics*

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In Section I, a new deduction for the Lorentz force is given by considering at first such molecules as have their nearest neighbor at a given distance, summing over all dipoles in the field, and finally averaging. In Section II, the same procedure is applied to the case that correlations between each molecule and its immediate neighborhood are assumed to exist according to Onsager's theory. The method leads to an extension of Onsager's results to the case of media of variable density, including gases. In Section III, the distribution law of the local field is deduced for dipoles of constant moment μ_0 with the aid of a probability theorem of Markoff-Gans. Both under Lorentz's and under Onsager's assumptions, the local field becomes isotropic, to a first approximation, for weak external fields. Its average value is $\bar{R}=16\pi n\mu_0/(27)^{\frac{1}{2}}$, i.e., more than twice the maximum value of the Lorentz force obtainable with a given dipole density n. In the last section the calculated deviations from the Clausius-Mosotti and Lorentz-Lorenz expressions are compared with experimental evidence.

INTRODUCTION

THE object of the following article is to apply two propositions in the calculus of probabilities to the analysis of the local field in polarized dielectrics. The first proposition is due to Hertz[1] and expresses, for a random distribution of points, the probability that any one of them has its nearest neighbor between given limits. The second theorem was originally proved by Markoff[2] for the two-dimensional case and then extended by Gans[3] to three dimensions. It permits a determination of the probability distribution of a sum of vectors if the probability distributions of the component vectors are known.

Both of the theorems have already been applied to similar problems,[4] but it seems to the author that their full usefulness has not been recognized. In particular, their joint application makes it possible to extend Gans' analysis and

* Part of the contents of this paper was presented at the meeting of the American Physical Society, February 23–24, 1940 (cf. Phys. Rev. **57**, 558 (1940)). The results then communicated were restricted to the case that no correlations between any one molecule and its immediate neighborhood were assumed to exist.

[1] P. Hertz, Math. Ann. **67**, 387 (1909).

[2] A. A. Markoff, *Wahrscheinlichkeitsrechnung* (German translation by H. Liebmann) (B. G. Teubner, Leipzig and Berlin, 1912), p. 173.

[3] R. Gans, Ann. d. Physik **50**, 163 (1916).

[4] R. Gans, reference 3; M. Reiche, Ann. d. Physik **50**, 1 (1916).

to eliminate a parameter, the nearest distance of approach between two molecules, from his results.

It must be emphasized that the two theorems, being merely propositions in the calculus of probabilities, do not contain any physical suppositions. Before applying these propositions it is necessary to determine on physical grounds which cases are to be considered as equally probable in the sense of the calculus. Therefore, the application can be made whether or not special correlations between neighboring molecules are assumed to exist. The latter assumption leads to the Lorentz force, the former is essential for the line of thought introduced by Onsager.[5]

I. The Lorentz Field

We shall begin by deducing the Lorentz force in a new way, one which avoids the difficulties connected with Lorentz's own deduction whereby the molecules inside the famous sphere are removed at first and then not sufficiently accounted for.

We shall consider a dielectric in a homogeneous field. In order to fix the ideas it will be assumed that the dielectric is contained in a parallel-plate condenser charged with "real charges" of the density $\pm\sigma$. Let the origin of a system of cylindrical coordinates r, φ, z be in the center of the condenser with the z axis at right angles to the plates. We shall assume a state of polarization in which there are n dipoles per cc distributed at random. Each is to have a moment μ, and all are to be directed at first along the z direction.* For the present it is irrelevant whether the dipoles are permanent or induced or both.

The mean force on unit charge inside the dielectric will be in the direction of z and may be resolved into two parts:

$$F_z = F_{1z} + F_{2z}, \tag{1.1}$$

the one, F_{1z}, being due to the real charges on the plates

$$F_{1z} = D_z = 4\pi\sigma, \tag{1.2}$$

and the second to the action of the dipoles.

In order to calculate F_{2z} we shall first fix our attention only on such molecules as have their nearest neighbor at distances between s and $s+ds$. The probability that this is the case is given by Hertz's formula

$$w(s)ds = 4\pi s^2 n e^{-4\pi s^3 n/3} ds. \tag{1.3}$$

As in an isotropic medium all directions of equal minimum separation are equally probable, the *average value* of F_{2z} on the dipoles now considered will be identical with the force on a unit charge in the center of a spherical cavity within the homogeneously polarized dielectric. It is, however, not legitimate to calculate this force from the surface charges which are equivalent to the polarization. This well-known procedure is perfectly sound in the case of the Lorentz sphere which is supposed to have a diameter large in comparison with molecular distances, but it is not adequate in our case where s decreases to molecular distances. Therefore we shall evaluate F_{2z} by a summation over all dipoles in the field. This procedure is not only the most direct, but also forms the basis for the higher approximations that will be performed in Section III.

Let $V(s)$ denote the volume bounded by the sphere of radius s and the plates of the condenser. Then we shall have

$$F_{2z} = n\int_{V(s)} \left(-\frac{\partial\phi}{\partial z}\right) dV, \tag{1.4}$$

where

$$\phi = \frac{\mu z}{(r^2+z^2)^{\frac{3}{2}}} \tag{1.5}$$

is the potential due to a dipole at the point r, φ, z.

The integrations are straightforward and singularities can be avoided by using cylindrical coordinates.* If the condenser is bounded by $r=R$ and $z=\pm H$, the result is

$$F_{2z} = 4\pi n\mu\left[\frac{1}{3} + \left(\frac{H}{(R^2+H^2)^{\frac{1}{2}}} - 1\right)\right] \tag{1.6}$$

where the terms in round brackets represent the influence of the external boundary of the field. They emphasize the fact that the force depends

[5] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936); J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937); C. J. F. Böttcher, Physica **5**, 635 (1938).

* Thermal agitation and the mutual interaction of the dipoles will be considered in Section III.

* The integration can also be extended to cavities of cylindrical and ellipsoidal shapes and leads to well-known results.

on the form of the external boundary (as, of course, of the cavity itself) and may be taken as an expression of the fact that the field is to be homogeneous. Whenever this is the case over a sufficiently extended area, it is possible to imagine a plate condenser with $H \ll R$ introduced in a suitable situation and charged with such a density $\pm\sigma$ that it produces the same homogeneous field in its interior. These charges, then, entirely replace the action of the remaining parts of the field in the static case. We shall, therefore, assume in all that follows that $H \ll R$.

We now have to multiply the value (1.6) by the probability (1.3) and to integrate over all values of s. As, however, (1.6) is independent of the value of s,* it is itself the average value. Putting $H \ll R$ in (1.6) and combining the result with (1.2) and the fundamental formula of electrostatics

$$\mathbf{D}=\mathbf{E}+4\pi\mathbf{P}, \tag{1.7}$$

we obtain Lorentz's formula

$$\mathbf{D}_z=\mathbf{E}_z+4\pi\mathbf{P}_z/3 \tag{1.8}$$

since the polarization is equal to μ in our case.

II. The Onsager Field

So far we have assumed that no special correlations between neighboring dipoles exist. Under these circumstances the application of Hertz's formula does not affect the material result. This is different if we follow Onsager[5] in considering the interaction between any one dipole and its immediate environment. We shall, throughout, adapt our deductions to Onsager's original treatment. This involves assigning to the dielectric its macroscopic dielectric constant ϵ down to molecular distances. Kirkwood[6] has improved Onsager's theory in this regard by considering the fluctuations of the local dielectric constant due to the discontinuous structure of the dielectric, but for our purpose it will suffice to start from Onsager's original formulae.

Again we shall consider such molecules at first as have their nearest neighbor at distances between s and $s+ds$. For the force acting on them we shall take Onsager's solution for the field inside a spherical cavity as modified by the presence of a dipole at the center of the cavity. If $\mathbf{F}$ signifies this field, then, for a molecule characterized by a polarizibility α and by a permanent electric moment μ_0, Onsager's deductions give

$$\mathbf{m}(s)=\frac{3\epsilon}{2\epsilon+1}\frac{\alpha}{1-\frac{2(\epsilon-1)}{2\epsilon+1}\frac{\alpha}{s^3}}\mathbf{E}+\frac{\mu_0}{1-\frac{2(\epsilon-1)}{2\epsilon+1}\frac{\alpha}{s^3}}\mathbf{u}$$

for the total moment, and, also, they give

$$\mathbf{F}(s)=\frac{3\epsilon}{2\epsilon+1}\frac{1}{1-\frac{2(\epsilon-1)}{2\epsilon+1}\frac{\alpha}{s^3}}\mathbf{E}+\frac{2(\epsilon-1)}{2\epsilon+1}\frac{\mu_0}{s^3}\frac{1}{1-\frac{2(\epsilon-1)}{2\epsilon+1}\frac{\alpha}{s^3}}\mathbf{u} \tag{2.2}$$

for the total field acting upon the molecule. Here $\mathbf{u}$ is a unit vector denoting the momentary orientation of μ_0.

Now the average has to be taken, but in doing so we have to consider the finite size of the molecules. Hertz's formula (1.3) holds only for points without extension. It is, however, easy to show (by an argument which is exactly analogous to the classical deduction of the van der Waals

* This statement is not correct, strictly speaking. If the nearest neighbor is to be found at a distance between s and $s+ds$, the probability of any other dipole being in a specified element of volume dV, is not ndV any more, but $ndV\cdot V/(V-v_0)$, where v_0 is the sphere of radius s. Consequently (1.6) ought to be multiplied by $V/(V-v_0)$ before the average is taken. This introduces, however, a correction that can be neglected. Furthermore, it must be borne in mind that the formula (1.3) is derived for points without extension (cf. p. 882).

[6] J. G. Kirkwood, J. Chem. Phys. 7, 911 (1939).

formula) that (1.3) is modified only in an insignificant way for the immediate neighborhood of any spherical molecule if its diameter is taken into account. But the constant, of course, has to be modified and (1.3) becomes

$$w(s)ds = 4\pi n s^2(\exp -(4\pi n/3)(s^3 - s_1^3))ds, \tag{2.3}$$

where s_1 is the nearest distance of approach for two molecules.

Multiplying (2.1) and (2.2) by (2.3) and integrating from s_1 to infinity, we find

$$\mathbf{m} = \overline{\mathbf{m}(s)} = \frac{3\epsilon}{2\epsilon+1}\varphi(z_1, q)\alpha\mathbf{E} + \mu\mathbf{u} \tag{2.4}$$

and

$$\mathbf{F} = \overline{\mathbf{F}(s)} = \frac{3\epsilon}{2\epsilon+1}\varphi(z_1, q)\mathbf{E} + \frac{\mu_0}{\alpha}q(\varphi(z_1, q) - 1)\mathbf{u}. \tag{2.5}$$

Here the new symbols have the following significance:

$$z_1 = 4\pi n s_1^3/3, \quad q = \frac{2(\epsilon-1)}{2\epsilon+1}\frac{4\pi n\alpha}{3}, \tag{2.6}$$

$$\mu = \mu_0\varphi(z_1, q). \tag{2.7}$$

The function $\varphi(z_1, q)$ is defined by

$$\varphi(z_1, q) = 1 - qe^{z_1 - q}Ei(q - z_1), \tag{2.8}$$

where

$$-Ei(-x) = \int_x^\infty \frac{e^{-t}}{t}dt \tag{2.9}$$

is the logarithmic integral which can be found in tables.[7]

Continuing now in exactly the same way as Onsager (in calculating the mean orientation), we find the polarization is

$$\mathbf{P} = n\left(\frac{\mu\mu^*}{3kT} + \frac{3\epsilon}{2\epsilon+1}\varphi(z_1, q)\alpha\right)\mathbf{E} \tag{2.10}$$

with

$$\mu^* = \frac{3\epsilon}{2\epsilon+1}\mu = \frac{3\epsilon}{2\epsilon+1}\varphi(z_1, q)\mu_0. \tag{2.101}$$

This leads to the final implicit formula for ϵ

$$\frac{\epsilon-1}{3} = \frac{4\pi n}{3}\frac{3\epsilon}{2\epsilon+1}\left(\frac{\mu^2}{3kT} + \varphi(z_1, q)\alpha\right), \tag{2.11}$$

which represents the extension of Onsager's result to dielectrics of variable densities down to densities of gases. Our Eqs. (2.5) and (2.10) represent, in this case, the connection between the external field, $\mathbf{E}$, the local field $\mathbf{F}$ and the polarization $\mathbf{P}$.

The characteristic function $\varphi(z_1, q)$ defined by (2.8) is always larger than 1. The d.c. ϵ becomes infinite for $q = z_1$ and this means for $z_1 = p$ where p is defined by

$$p = \frac{4\pi n\alpha}{3}. \tag{2.12}$$

[7] E. Jahnke and F. Emde, *Funktionentafeln mit Formeln und Kurven* (Ed. 2 with English text, B. G. Teubner, Leipzig, 1933).

This result coincides with Lorentz's ($\epsilon \to \infty$ for $p \to 1$) only if we put $z_1 = 1$, as is sometimes done for liquids. The value $\epsilon \to \infty$ is approached by (2.11) from the side of $p > z_1$, and the dependance of ϵ on density comes out somewhat different from the Lorentz law even for nonpolar substances.

For $p < 1$ we can develop (2.11) into a series finding for nonpolar substances

$$\frac{\epsilon-1}{3} = p[1+p+(2A_1-1)p^2+(2A_1-1)p^3+\cdots] \tag{2.13}$$

where

$$A_1 = e^{z_1}(-Ei(-z_1)). \tag{2.14}$$

Introducing the molar polarization

$$P_0 = \frac{4\pi N\alpha}{3} \tag{2.15}$$

(N = Avogadro's number) and the molar volume v, we find that the Clausius-Mosotti expression becomes

$$\frac{\epsilon-1}{\epsilon+2}v = P_0\left[1+2(A_1-1)\left(\frac{P_0}{v}\right)^2+2(1-A_1)\left(\frac{P_0}{v}\right)^3+\cdots\right]. \tag{2.16}$$

In order to compare our results with Onsager's, we must take some average value of s_1 adapted to liquids. If we define the optical dielectric constant by $(\epsilon_0-1)/(\epsilon_0+2) = p$ and neglect terms of the second order in (ϵ_0-1), our formula (2.11) becomes identical with the corresponding formula of Onsager provided we choose $A_1 = 1$ (corresponding to $z_1 = 0.435$) and substitute our ϵ_0 for his n^2.

We might also point out the *formal* similarity of our results with those of Kirkwood's modification of Onsager's theory, but it must be emphasized that his treatment is superior to ours as to the atomistic foundation. Our formula (2.7), however, establishes a more general connection between the actual electric moment μ at variable densities and the moment in vacuum μ_0.

III. The Local Field

Our previous treatment is concerned only with the mean value of F. In order to establish how the values of the components of the local field spread about their mean values if thermal agitation and the mutual interaction of the dipoles are taken into account, we shall apply the theorem of Markoff and Gans mentioned in the introduction. In our case the component vectors are the fields produced at the location of one particular dipole A by all other dipoles B_i. In order that these components may be known, the fields at the locus of the other dipoles must first be determined. The problem can be solved in the usual way by successive approximations if one starts with some suitable assumption regarding the probability distribution of the dipoles B_i and finds, with the aid of the M-G theorem, a first approximation for the probability distribution of the local field acting on A. Subjecting, now, the dipoles B_i to the local field so found, one calculates, by a second application of the theorem, a second approximation for the local field at A, and so on.

We shall apply this procedure to the case of permanent dipoles only, though it can be extended to polarizable molecules as well.[8] Since the statement of the M-G theorem and the calculations involved are somewhat lengthy, we refer for the details to the paper of Gans[2] and state only the results.

For a zero approximation we shall take a Langevin distribution in a suitably chosen field **G**. In particular, if no correlations between neighboring molecules are assumed, it is most natural to take for **G** the constant external field E_z, though this choice may unfavorably affect the convergence of the procedure. Under these assumptions the probability for any of the dipoles B_i to be directed

[8] R. Gans, Ann. d. Physik **64**, 481 (1921).

within the elementary solid angle $\sin\chi d\chi d\psi$ (χ being the angle between the dipole and the field) is given by

$$w_1 \sin\chi d\chi d\psi = \frac{1}{2\pi}\frac{\xi}{e^{\xi}-e^{-\xi}} e^{\xi\cos\chi}\sin\chi d\chi d\psi, \tag{3.1}$$

where

$$\xi = \mu_0 E_z/kT. \tag{3.2}$$

Let us first choose for the dipole A, one which is separated from its nearest neighbor by a distance between s and $s+ds$. The probability, then, that the components of the resultant field at A are within the limits X and $X+dX$, Y and $Y+dY$, Z and $Z+dZ$ is found to be*

$$w_2 dX dY dZ = \frac{\exp\left(-X^2/2a_{11} - Y^2/2a_{22} - (Z-a_3)^2/2a_{33}\right)}{(8\pi^3 a_{11}a_{22}a_{33})^{\frac{1}{2}}} dX dY dZ, \tag{3.3}$$

where the coefficients are given by

$$a_3 = -\frac{8\pi n\mu_0}{3} L(\xi), \tag{3.31}$$

$$a_{11} = a_{22} = \frac{4\pi n\mu_0^2}{5s^3}\left[1+\frac{1}{3\xi}L(\xi)\right], \tag{3.32}$$

and

$$a_{33} = \frac{4\pi n\mu_0^2}{5s^3}\left[\frac{4}{3}-\frac{2}{3\xi}L(\xi)\right]. \tag{3.33}$$

Here and in all that follows $L(\xi)$ represents the Langevin function.

From (3.3) follows (keeping s constant)

$$\bar{X}=0, \quad \bar{Y}=0, \quad \bar{Z}=a_3. \tag{3.4}$$

Since these expressions are independent of s, they also hold if averaged over s. The third of these equations leads to the Lorentz formula (1.8) as

$$P_z = n\mu_0 L(\xi). \tag{3.5}$$

The means, however, of the resultant field, $\bar{R}=\overline{(X^2+Y^2+Z^2)^{\frac{1}{2}}}$ and of its component at right angles to the external field, $\bar{R}_0=\overline{(X^2+Y^2)^{\frac{1}{2}}}$, involve s, as does also the distribution function (3.3) itself. We therefore multiply (3.3) by its probability (1.3), integrate, and find as the final expression for the first approximation to the local field

$$w_2' dX dY dZ = \frac{1}{(8(a_{11}')^2 a_{33}')^{\frac{1}{2}}}\frac{1}{W^{5/2}} dX dY dZ. \tag{3.6}$$

Here we have put

$$a_{11}' = a_{11}s^3, \quad a_{33}' = a_{33}s^3, \tag{3.61}$$

and

$$W = \frac{4\pi n}{3} + \frac{X^2+Y^2}{2a_{11}'} + \frac{(Z-a_3)^2}{2a_{33}'}. \tag{3.62}$$

The contribution of the irregular part of the local field will be the more important the weaker the external field and the higher the temperature. We shall, therefore, calculate $\bar{R}$ only for the limiting

* In calculating Gans' coefficients a_i, which are linear averages, cylindrical coordinates have been used as in Section I. However, in calculating the quadratic averages a_{ij}, spherical coordinates may be used more conveniently because the integrand is $\propto 1/r^4$ and, therefore, the result is independent of the shape of the external boundary.

case $\xi \to 0$. Then we have from (3.32) and (3.33) in combination with (3.61)

$$a_{11}' = a_{33}' = 8\pi n\mu_0^2/9, \quad \xi \ll 1. \tag{3.7}$$

Furthermore, in this case, a_3 becomes negligible compared with Z, so that the distribution functions (3.3) and (3.6) are isotropic for sufficiently weak external fields and sufficiently high temperatures. Taking the average we obtain

$$\bar{R} = \frac{4}{\sqrt{3}} \frac{4\pi n\mu_0}{3}. \tag{3.8}$$

As $4\pi n\mu_0/3$ is the *maximum value* which the Lorentz force (apart from the external force) can assume for a given value of n, (3.8) shows that the mean value of the resultant local force is more than twice this maximum value. The actual Lorentz force as given by (1.8) and (3.5) is small in the case of a weak external field; therefore, the ratio of the resultant local force to the Lorentz force can become large for sufficiently large values of $n\mu_0$. All directions are, under our present assumptions, equally probable for the resultant local force.

If we now want to extend the analysis of the local field to the case of Onsager's theory we have to give up the assumption that the field **G** orienting the dipoles B_i is unaffected by the presence of the dipole A. We, therefore, now take for the field **G** the external field as modified by the spherical cavity of radius s around A. Consequently, we put

$$\mathbf{G} = -\operatorname{grad} \psi, \quad \psi = -(E_z + M/r^3)z, \tag{3.9}$$

where

$$M = \frac{\epsilon - 1}{2\epsilon + 1} s^3. \tag{3 10}$$

In applying the M-G theorem now, we restrict ourselves to the case of weak external fields because the Onsager solution (3.9) holds only for a case of a constant ϵ. In this case the integrations are easily performed and it is found that the coefficients a_{11}, a_{22}, a_{33} retain the values given by (3.61) and (3.7) except that a_3 is changed to

$$a_3 = -\frac{8\pi n\mu_0}{3} \frac{3\epsilon}{2\epsilon + 1} \frac{\xi}{3}. \tag{3.11}$$

Thus it is seen that the probability distribution of the local field (for $\xi \ll 1$) represented by Eqs. (3.3) and (3.6) with the coefficients (3.7) still holds in the case of the Onsager theory with only the alteration of the mean value $\bar{Z}$.

To the same approximation (neglecting also a term of the order s^3/V) we find

$$P_z = n\mu_0 \xi/3 \tag{3.12}$$

and, consequently,

$$F_z = E_z + 4\pi P_z + a_3 = \frac{3\epsilon}{2\epsilon + 1} E_z, \tag{3.13}$$

which is identical with Onsager's value (and our formula (2.5)) for $\alpha = 0$.

Our evaluations so far concern only the first approximation of the procedure indicated on page 883. For the higher approximations the integrations become rather involved in the general case. The author has carried through the calculation of a_3 to a second approximation with only the simplification that the slight difference between a_{11} and a_{33} (see (3.32) and (3.33)) is disregarded and that no correlations between neighbors are assumed. He then finds, instead of (3.5)

$$P_z = n\mu_0 \left[\frac{\mu_0 (E_z + (4\pi n\mu_0/3) L(\xi))}{kT} \right]. \tag{3.14}$$

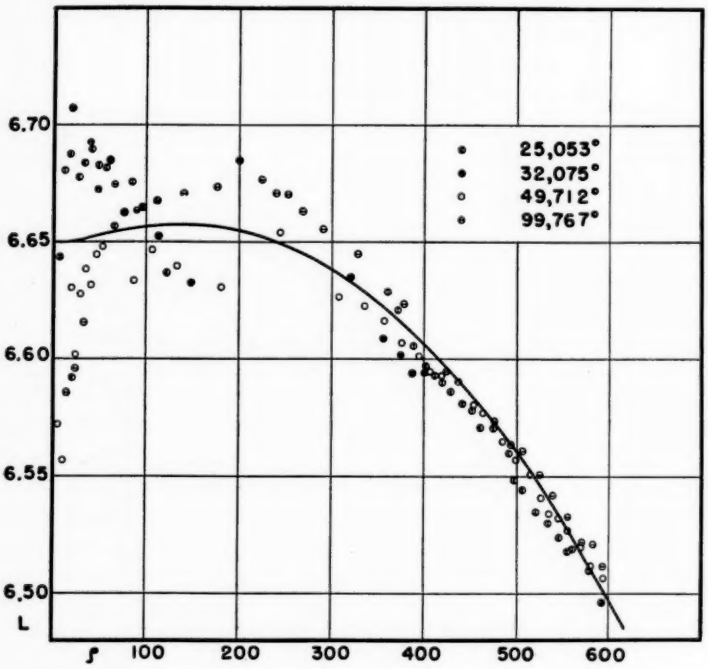

FIG. 1. The diagram represents L, the Lorentz-Lorenz function of CO_2 for $\lambda=5876$A in function of the Amagat density ρ. The curve is calculated from Eq. (2.16) with the values $P_0=6.65$ and $\delta=\frac{1}{6}$. The points correspond to observations of Michels and Hamers for four different temperatures.

If, however, only small values of the external field are considered, it can be shown that the evaluation of $a_3^{(m+1)}$ (i.e., the $(m+1)$ approximation) requires only a previous knowledge of $a_3^{(m)}$. We shall again distinguish between the two former cases. If no correlations are assumed, the integration yields

$$a_3^{(m+1)}=-2p'[\epsilon E_z+a_3^{(m)}], \tag{3.15}$$

where

$$p'=4\pi n\mu_0^2/9kT. \tag{3.16}$$

This recurrence formula ultimately leads to

$$F_z=E_z(1+p'+(p')^2+\cdots)=E_z/(1-p') \tag{3.17}$$

and

$$\epsilon=1+3p'(1+p'+(p')^2+\cdots)=1+3p'/(1-p') \tag{3.18}$$

which is exactly the Lorentz formula.

If, however, correlations are assumed to exist, as above, the influence of the cavity has to be taken into account in every step. It is then found that

$$a_3^{(2)}=\frac{3\epsilon}{2\epsilon+1}a_3^{(1)}, \quad a_3^{(m+1)}=a_3^{(m)} \quad \text{for } m\geqslant 2. \tag{3.19}$$

As we get at the same time

$$P_z^{(2)}=\frac{3\epsilon}{2\epsilon+1}P_z^{(1)}, \quad P_z^{(m+1)}=P_z^{(m)} \quad \text{for } m\geqslant 2, \tag{3.20}$$

the average values do not change any more after the second approximation and the value (3.13) for the Onsager field holds throughout.

IV. Comparison with Experimental Evidence

Our extension of the Onsager theory leads us to expect a dependence of the Clausius-Mosotti expression upon density even for nonpolar substances. This is best seen from formula (2.16). It should be noted, however, that the coefficient A_1 is still a function of the density, z_1 being proportional to n. If we put

$$\delta = p/z_1 = \alpha/s_1^3, \tag{4.1}$$

the Cl-M expression depends on δ in addition to the usual dependence on P_0 and v. Since A_1 becomes large for small values of z_1 and approaches zero for large values of z_1, the second term on the right-hand side of (2.16) changes sign for $A_1=1$, and the Cl-M expression will initially rise with increasing density and then pass through a maximum.

This is exactly the behavior shown by the results of the most extended measurements: those of Michels and Kleerekoper[9] on CO_2. These measurements, however, indicate an influence of temperature which is not accounted for by our formula; and if one tries to represent the experimental data quantitatively, it is seen that (2.16) yields too low a minimum, at least for admissible values of δ. According to the evidence from the equation of state, δ ought to be of the order of 0.1 as pointed out by Kirkwood,[10] whereas our formula gives a maximum of only 1 percent for $\delta \sim 0.5$. However, the deviations from the Cl-M law due to the difference between the Lorentz and Onsager fields are not the only ones which are to be expected. The so-called "translational fluctuations," which were calculated first by Keyes and Kirkwood,[10] lead to a formula which is very similar to (2.16) and accounts for the observed maximum more completely for reasonable values of δ, giving, at the same time, a temperature dependence in the observed direction. Furthermore, the molecules will surely be deformed at high densities, as suggested by Michels, de Boer and Bijl.[11]

Measurements of Michels and Hamers[12] on the refractive index of CO_2 up to pressures of 2.400 atmos. and Amagat densities $\rho_A=600$, show, however, a distinctly different behavior. There does not seem to be a very marked maximum of the Lorentz-Lorenz expression, but rather a

[9] A. Michels and L. Kleerekoper, Physica **6**, 586 (1939).

[10] F. G. Keyes and J. G. Kirkwood, Phys. Rev. **37**, 202 (1931); J. G. Kirkwood, J. Chem. Phys. **4**, 592 (1936); J. H. Van Vleck, J. Chem. Phys. **5**, 556 (1937); **5**, 991 (1937).

[11] A. Michels, J. de Boer and A. Bijl, Physica **4**, 981 (1937).

[12] A. Michels and J. Hamers, Physica **4**, 995 (1937).

Table I. *Comparison of dipole moments as calculated by Böttcher from data of the pure liquids with those calculated from formula (2.11).*

		$\mu_0 \cdot 10^{18}$ Calculated by Böttcher		$\mu_0 \cdot 10^{18}$ Calculated from (2.11)		$\mu_0 \cdot 10^{18}$ Vapor (Average)	δ
Benzonitrile	t	0	70	0	70	4.39	0.250
	μ_0	3.58	3.76	4.26	4.40		
Methyl bromide	t	−100	0	−100	0	1.77	0.319
	μ_0	1.57	1.63	1.77	1.77		
Methyl iodide	t	−70	40	−70	40	1.54	0.298
	μ_0	1.29	1.36	1.52	1.54		
Ethyl bromide	t	−90	30	−90	30	2.00	0.392
	μ_0	1.80	1.91	1.96	2.00		
Ethyl iodide	t	−90	70	−90	70	1.86	0.283
	μ_0	1.52	1.71	1.83	1.88		
Chlorobenzene	t	10	132	10	132	1.70	0.321
	μ_0	1.50	1.57	1.69	1.70		

most distinct decrease for densities above $\rho_A \sim 100$ (this decrease being maximally 2.3 percent). Furthermore, there is no decided influence of the temperature, at least not for high densities. This behavior is brought out very well by our formula. In Fig. 1 we have compared the experimental data with a theoretical curve calculated from (2.16) with the values $P_0 = 6.65$ and $\delta = \frac{1}{6}$. (Some experimental points have been omitted.) The agreement is very satisfactory in the region where the experimental uncertainty is small, and the value of δ seems reasonable.

It might appear strange, at first sight, that the behavior of the dielectric constant is expressed better by Kirkwood's theory, and that of the refractive index, better by ours. This is, however, what might be expected on closer examination. Our deduction assumes the molecules to be fixed in a random distribution (which gives rise to a probability distribution in s), whereas in Kirkwood's deduction the average over all distributions in configuration and momentum space is taken. Now, for the short duration of a light wave, the molecules may be considered at rest in their random distribution, and this gives rise to the fluctuations due to the variations of s. If, however, the dielectric constant is measured, this influence will be canceled out and replaced by the influence of the thermal agitation.

With respect to the behavior of polar liquids we have already pointed out the fact that our formulae become identical with Onsager's for low values of the polarizability if A_1 is assigned a suitable constant value. Consequently, the general results of Onsager's concerning the absence of a "$4\pi/3$ catastrophe," the agreement with Wyman's empirical relation, etc., remain unaltered.

A more detailed test of Onsager's theory has recently been made by Böttcher,[13] who calculated the dipole moments of the free molecule from data of the pure dipole liquids. He found that the moments thus calculated are "sufficiently independent of the temperature" and show a remarkable agreement with values determined in gases and dilute solutions. It is to be expected that the agreement between the theory and experiment can be improved by the use of our formula (2.11) as this formula still contains δ as a disposable constant. The author has examined this point and has found the results to confirm the expectation with certain restrictions.

First of all, Böttcher's group of three "associating compounds" has to be excluded. For such substances, as shown by Kirkwood[6] in the case of water, a more detailed knowledge of the correlation between neighboring molecules than given by the Onsager field is required. Among the other substances of Böttcher's list, there is a small group (4 out of 29) which behaves abnormally, inasmuch as the calculated values of μ_0 decrease with rising temperature and (in 3 out of 4 cases) are too large in comparison with the values for the vapors. In these cases no improvement can be obtained by our formula (2.11) unless δ is assigned values which are unacceptably large (δ from 0.8 to 1.0). Böttcher has already pointed out that a deformation of the molecule may account for the abnormal behavior of this group.

In all other cases the values calculated by Böttcher increase with rising temperature, and, at the same time, in quite a number of cases, μ_0 is found to be smaller for the liquids than for the vapors. For this whole group, wherever it seems desirable, a marked improvement can be obtained by the application of (2.11). The values of δ which have to be chosen seem still somewhat large but admissible (δ from 0.25 to 0.5). A few cases where the observed temperature intervals are large and the improvements particularly noticeable are given in Table I. There still remains a marked tendency of the calculated μ_0 values to increase with temperature. This systematic deviation is in such a direction that it would be accounted for by the assumption that δ increases (i.e., the smallest distance of approach between two molecules decreases) with rising temperature. The deviation, however, is too insignificant to warrant such a conclusion.

[13] C. J. F. Böttcher, Physica **6**, 59 (1939).

Dielectric Polarization in Solution

II. The Polarization of Some Alcohols as a Function of Concentration and Temperature

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(Received July 8, 1940)

Curves showing the apparent molal polarization as calculated by the Debye-Clausius-Mosotti procedure are compared with the molal polarizability calculated as proposed in the introductory paper of this series. It is possible to give a satisfactory explanation of the latter curves in terms of association whereas the former curves show a behavior so complex that it is difficult to interpret. In the first paper of this series the authors showed that the behavior of the apparent molal polarization as calculated by the Debye-Clausius-Mosotti procedure was such as to lead to dubious conclusions even for the simplest type of polar substances. A procedure of applying the equation of Onsager was outlined which promises to make possible the interpretation of data on polarization in a realistic manner. The first paper was inspired by an attempt to apply the Debye-Clausius-Mosotti procedure to the alcohols in solution where it leads to results that are puzzling indeed. In this paper these data are published and discussed from the standpoint of the Onsager theory. When some additional data on alcohols in very dilute solution are obtained, it is hoped that an exact value can be obtained for the moments of the alcohols.

RECENT studies[1] have shown that alcohols are associated to a very high degree even in inert solvents and it seems clear that the high dielectric constant is dependent upon the formation of long chain polymers. In order to understand the behavior of the polar liquids it is, therefore, important to study the dependence of polarization upon degrees of polymerization. The solvent used for these studies was carbon tetrachloride since this was the solvent used in the infra-red study cited above.

Our results for the behavior of alcohols in this solvent is forecast by the work of Stranathan.[2] Smyth[3] has obtained similar results for various alcohols in solvents such as benzene and hexane. The most recent work appears to be that of Henning,[4] who found the polarization of the alcohols to vary greatly with the concentration in various solvents. The authors hope in this research to show a correlation between the variation in polarization and the degree of association as shown by infra-red absorption.

A. Apparatus

The heterodyne beat method was used to measure the dielectric constants of the solutions. The design of the apparatus is identical with that described by Stranathan except for the following changes: A 2E5 radio tube was used to adjust the frequency of the variable oscillator instead of a thousand-cycle microphone hummer with electrical output, thus eliminating the power pack necessary to drive it; a Bakelite panel was substituted for the hard rubber panel used by Stranathan; and the tank circuit of the Hartley oscillator was modified to contain a 500-$\mu\mu$f General Radio variable condenser, the test cell, and a type 722-F General Radio precision condenser connected in parallel. The 2E5 tube was found to be more convenient and capable of greater sensitivity than the telephone receiver. The temperature of the crystal was controlled to insure constant frequency.

Various types of test cell were used in this work. The most satisfactory type of cell has been found to be one similar to the cell used by Smyth.[5] It consists of three concentric cylindrical platinum electrodes sealed in glass. The three terminals are brought out in a symmetrical arrange-

[1] A. M. Buswell, V. Deitz and W. H. Rodebush, J. Chem. Phys. **5**, 501 (1937).
[2] J. D. Stranathan, Phys. Rev. **31**, 653 (1928).
[3] C. P. Smyth, Am. Chem. Soc. Monograph, *Dielectric Constant and Molecular Structure* (Chemical Catalog Company, New York, 1931).
[4] C. Henning, Zeits. f. physik. Chemie **B28**, 269 (1935).
[5] Smyth and Morgan, J. Am. Chem. Soc. **50**, 1547 (1928).

ment so that the capacity of the cell can be varied without changing the electrical circuits and in this way the end effects can be estimated.

B. Procedure

The measurement of the dielectric constants of the various solutions was carried out in the following manner: A solution of a given concentration was prepared by weighing the components in a specific gravity bottle. The solution was placed in the test cell which had been previously cooled to about −10°C and the dielectric constant determined at approximately ten-degree intervals until a temperature of 50°C was reached. Ten solutions, varying in concentration from approximately 0.005 to 0.15 mole fraction of the polar substance were measured in a similar manner for each compound. The values of the dielectric constant of each solution were then plotted *versus* temperature, smooth curves drawn, and the dielectric constant read at ten-degree intervals from −10° to 50°C. The data were then plotted as dielectric constant *versus* composition, smooth curves were drawn and the final results adjusted to these curves.

The densities of the various solutions were determined with a calibrated pycnometer at 0°, 20° and 40°C. The densities at the other temperatures were obtained by interpolation or extrapolation.

Materials

Benzene.—Thiophene-free benzene was shaken with sulfuric acid until no coloration appeared, washed with water, with dilute sodium carbonate solutions, distilled, fractionally crystallized and dried over phosphorus pentoxide and sodium and fractionated.

Carbon tetrachloride.—Technical grade was saturated with chlorine and exposed to sunlight for eight days, washed with sodium hydroxide and sodium acid sulfite, water, then dried over phosphorus pentoxide and fractionally distilled: b.p. 76.7–76.8/757 mm, K^{20} 2.2355, d_{20}^{20} 1.5935.

Methyl alcohol, b.p. 64.7–64.8/743 mm; *n*-butyl alcohol, b.p. 116.9–117.0/744 mm; *sec.*-butyl alcohol, b.p. 99.0–99.1/747 mm; cyclohexanol, b.p. 159.4–159.5/735 mm; Cellosolve, b.p. 132.0–132.1/745.1 mm and propylene glycol monoethyl ether, b.p. 158.2–158.7/746 mm were dried by suitable drying agents and fractionally distilled. The sample of *test*-butyl alcohol (b.p. 82.29°) was supplied by the Shell Development Company as being of high purity.

Calibration of the cell

The primary object of this study was not to establish absolute values for the dielectric constant but rather to obtain reproducible values at different concentrations and temperatures. The chief difficulty is found in the calibration of the cell. A search of the literature discloses a satisfactory agreement upon the values of the dielectric constant for very few substances. Benzene is the only substance for which the values seem to be established with sufficient accuracy. In calibrating the cell we used the value obtained by Hartshorn and Oliver,[6] 2.2825 at 20°C. In order to correct for the capacity due to end effects in the cell it was necessary to determine the capacity of the cell filled with air following the procedure of Davies.[7]

While this procedure is satisfactory for the calibration at 20°C the calibration at other temperatures offers difficulties which cannot be overcome in an entirely satisfactory manner. Hartshorn and Davies measured the dielectric constant of benzene over the range from 12–22°C but this is too short a range for extrapolation. There are no values in the literature either for benzene or for other substances over a temperature range of 60° which can be considered dependable. As a first approximation one may assume the capacity of the cell used to be independent of temperature, but this neglects the change in dielectric constant of the cell material and the possibility of unsymmetrical expansion. The procedure we followed was to measure the capacity of the cell filled with air at different temperatures and to assume that the change in capacity was entirely due to the cell itself. This procedure neglects the change in end capacity. The end capacity is, however, only a few percent of the total capacity and the calibration obtained in this way agrees with the results of Hartshorn and Oliver mentioned above over the limited

[6] L. Hartshorn and D. A. Oliver, Proc. Roy. Soc. **A123**, 664 (1929).

[7] R. M. Davies, Phil. Mag. **21**, 1 (1936).

TABLE I. *n-butyl alcohol in carbon tetrachloride. Dielectric constants and densities of solutions at temperatures of −10°C to 50°C.*

N_2	0.00000	0.0045214	0.0072181	0.010871	0.018435	0.035384	0.051015	0.069756	0.086139	0.11801	0.14159
Temp. °C											
ϵ	2.2958	2.3125	2.3204	2.3290	2.3432	2.3771	2.4090	2.4524	2.4997	2.6180	2.7290
−10 d.	1.6510	1.6472	1.6451	1.6422	1.6360	1.6224	1.6097	1.5947	1.5817	1.5587	1.5391
ϵ	2.2757	2.2920	2.3001	2.3093	2.3253	2.3616	2.3956	2.4399	2.4871	2.6022	2.7078
0 d.	1.6318	1.6282	1.6260	1.6231	1.6171	1.6038	1.5912	1.5763	1.5633	1.5405	1.5214
ϵ	2.2555	2.2716	2.2798	2.2895	2.3070	2.3462	2.3820	2.4272	2.4739	2.5864	2.6866
10 d.	1.6128	1.6090	1.6069	1.6040	1.5982	1.5848	1.5725	1.5577	1.5449	1.5224	1.5037
ϵ	2.2355	2.2509	2.2594	2.2697	2.2890	2.3306	2.3686	2.4143	2.4611	2.5706	2.6650
20 d.	1.5936	1.5899	1.5878	1.5852	1.5791	1.5658	1.5538	1.5393	1.5266	1.5043	1.4860
ϵ	2.2155	2.2304	2.2393	2.2502	2.2711	2.3155	2.3550	2.4017	2.4485	2.5548	2.6440
30 d.	1.5744	1.5709	1.5687	1.5660	1.5600	1.5471	1.5352	1.5208	1.5082	1.4862	1.4683
ϵ	2.1954	2.2101	2.2191	2.2300	2.2511	2.2978	2.3389	2.3871	2.4338	2.5375	2.6230
40 d.	1.5552	1.5517	1.5495	1.5469	1.5410	1.5283	1.5164	1.5023	1.4901	1.4680	1.4506
ϵ	2.1754	2.1889	2.1973	2.2081	2.2292	2.2768	2.3194	2.3720	2.4167	2.5189	2.6012
50 d.	1.5358	1.5325	1.5305	1.5277	1.5219	1.5093	1.4977	1.4839	1.4718	1.4498	1.4328

TABLE II. *sec.-butyl alcohol in carbon tetrachloride. Dielectric constants and densities of solutions at temperatures of −10° to 50°C.*

N_2	0.00000	0.0058110	0.010201	0.016468	0.032899	0.057845	0.084932	0.11882	0.14400
Temp. °C									
ϵ	2.2957	2.3185	2.3315	2.3465	2.3797	2.4243	2.4755	2.5552	2.6170
−10 d.	1.6506	1.6456	1.6420	1.6372	1.6241	1.6040	1.5828	1.5563	1.5368
ϵ	2.2757	2.2980	2.3114	2.3267	2.3625	2.4113	2.4654	2.5470	2.6092
0 d.	1.6316	1.6267	1.6231	1.6183	1.6051	1.5852	1.5641	1.5378	1.5183
ϵ	2.2557	2.2770	2.2904	2.3066	2.3453	2.3984	2.4554	2.5387	2.6013
10 d.	1.6125	1.6076	1.6040	1.5993	1.5862	1.5665	1.5454	1.5193	1.4998
ϵ	2.2356	2.2560	2.2695	2.2865	2.3277	2.3857	2.4454	2.5306	2.5937
20 d.	1.5935	1.5885	1.5850	1.5803	1.5673	1.5478	1.5267	1.5008	1.4813
ϵ	2.2154	2.2348	2.2483	2.2665	2.3107	2.3727	2.4353	2.5224	2.5862
30 d.	1.5745	1.5697	1.5660	1.5613	1.5488	1.5290	1.5080	1.4824	1.4628
ϵ	2.1953	2.2140	2.2270	2.2449	2.2909	2.3562	2.4222	2.5107	2.5748
40 d.	1.5553	1.5507	1.5469	1.5423	1.5293	1.5101	1.4893	1.4639	1.4443
ϵ	2.1750	2.1930	2.2060	2.2235	2.2679	2.3353	2.4041	2.4933	2.5610
50 d.	1.5362	1.5315	1.5279	1.5232	1.5103	1.4913	1.4705	1.4454	1.4258

temperature range so that it seems unlikely that a significant error can be introduced into the comparison at different temperatures.

The value obtained for the dielectric constant of carbon tetrachloride was 2.2355 at 25°C. It has been found in this laboratory that carbon tetrachloride is extremely difficult to purify, one of the impurities difficult to remove being chloroform. A wide variety of results are given in the literature, the best work apparently being that of Davies who found the value 2.2360. Extraordinary precautions were taken to exclude moisture in this work and it was observed that carbon tetrachloride saturated with water has a dielectric constant 0.1 greater than the dry liquid.

RESULTS

The data upon dielectric constant and density for several alcohols are presented in Tables I–VI. In Fig. 1 are shown the apparent molal polarization curves for cyclohexanol as calculated by the Debye-Clausius-Mosotti procedure. These curves

TABLE III. *tert.-butyl alcohol in carbon tetrachloride. Dielectric constants and densities of solutions at temperatures of −10°C to 50°C.*

N_2	0.00000	0.0045368	0.0088019	0.014684	0.028341	0.052581	0.076888	0.11368	0.13905
Temp. °C									
ϵ	2.2963	2.3138	2.3258	2.3382	2.3608	2.3845	2.4116	2.4527	2.4803
−10 d.	1.6510	1.6470	1.6432	1.6384	1.6271	1.6064	1.5860	1.5552	1.5331
ϵ	2.2758	2.2922	2.3050	2.3188	2.3472	2.3758	2.4078	2.4542	2.4897
0 d.	1.6320	1.6279	1.6241	1.6192	1.6080	1.5874	1.5671	1.5367	1.5148
ϵ	2.2556	2.2712	2.2843	2.3001	2.3329	2.3673	2.4038	2.4566	2.4980
10 d.	1.6128	1.6088	1.6051	1.6001	1.5889	1.5684	1.5483	1.5181	1.4966
ϵ	2.2355	2.2502	2.2634	2.2808	2.3171	2.3575	2.3993	2.4591	2.5036
20 d.	1.5936	1.5897	1.5860	1.5809	1.5699	1.5495	1.5295	1.4996	1.4784
ϵ	2.2155	2.2297	2.2426	2.2600	2.2993	2.3461	2.3926	2.4585	2.5063
30 d.	1.5745	1.5707	1.5670	1.5619	1.5508	1.5305	1.5108	1.4809	1.4601
ϵ	2.1956	2.2085	2.2209	2.2380	2.2785	2.3313	2.3819	2.4535	2.5057
40 d.	1.5554	1.5517	1.5480	1.5428	1.5318	1.5116	1.4919	1.4623	1.4417
ϵ	2.1757	2.1870	2.1978	2.2146	2.2537	2.3105	2.3648	2.4413	2.5020
50 d.	1.5364	1.5327	1.5290	1.5238	1.5128	1.4927	1.4732	1.4437	1.4233

TABLE IV. *Cyclohexanol in carbon tetrachloride. Dielectric constants and densities of solutions at temperatures of −10°C to 50°C.*

N_2	0.00000	0.0054342	0.012042	0.017630	0.032243	0.047586	0.062930	0.081921	0.12768
Temp. °C									
ϵ	2.2963	2.3195	2.3417	2.3569	2.3912	2.4290	2.4738	2.5371	2.7144
−10 d.	1.6510	1.6467	1.6420	1.6380	1.6277	1.6170	1.6058	1.5922	1.5598
ϵ	2.2758	2.2980	2.3215	2.3383	2.3749	2.4142	2.4600	2.5241	2.6943
0 d.	1.6320	1.6277	1.6228	1.6190	1.6088	1.5983	1.5873	1.5740	1.5422
ϵ	2.2556	2.2768	2.3014	2.3200	2.3589	2.4000	2.4465	2.5106	2.6745
10 d.	1.6128	1.6088	1.6040	1.6000	1.5900	1.5795	1.5688	1.5557	1.5247
ϵ	2.2355	2.2556	2.2813	2.3009	2.3429	2.3856	2.4329	2.4957	2.6548
20 d.	1.5936	1.5895	1.5848	1.5810	1.5712	1.5608	1.5504	1.5374	1.5072
ϵ	2.2155	2.2346	2.2600	2.2808	2.3254	2.3692	2.4185	2.4791	2.6351
30 d.	1.5745	1.5705	1.5660	1.5621	1.5523	1.5421	1.5320	1.5192	1.4896
ϵ	2.1956	2.2137	2.2380	2.2589	2.3056	2.3534	2.4015	2.4599	2.6144
40 d.	1.5554	1.5516	1.5471	1.5432	1.5335	1.5234	1.5135	1.5008	1.4720
ϵ	2.1757	2.1915	2.2148	2.2346	2.2820	2.3313	2.3798	2.4386	2.5917
50 d.	1.5364	1.5326	1.5280	1.5243	1.5147	1.5048	1.4950	1.4825	1.4545

show a maximum in dilute solutions which is more pronounced for cyclohexanol but which is shown to a greater or less degree by all of the heavier alcohols. This maximum has been observed by other investigators so that it is not to be explained by experimental error. In the authors' opinion, this maximum cannot be explained upon any reasonable assumption and, therefore, must be due to the failure of the Clausius-Mosotti equation and hence illusory.

On the other hand, if we plot what we have chosen to call the molal polarizability

$$\frac{\epsilon-1}{4\pi}\left(\frac{N_1M_1+N_2M_2}{d}\right)$$

for the alcohols (Figs. 2, 3, 4, 5), we find a behavior that appears at once simple and understandable. In the first paper of this series we showed that according to the theory of Onsager[8] this quantity should be and is linear with

[8] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).

TABLE V. *2-ethoxyethanol-1 in carbon tetrachloride. Dielectric constants and densities of solutions at temperatures of −10°C to 50°C.*

N_2	0.00000	0.0064984	0.0096897	0.019603	0.040410	0.055324	0.081563	0.10852	0.13598
Temp. °C									
ε	2.2962	2.3460	2.3685	2.4364	2.5721	2.6688	2.8461	3.0359	3.2471
−10 d.	1.6507	1.6460	1.6437	1.6368	1.6221	1.6114	1.5929	1.5743	1.5553
ε	2.2759	2.3225	2.3445	2.4098	2.5407	2.6352	2.8075	2.9894	3.1915
0 d.	1.6316	1.6270	1.6248	1.6178	1.6033	1.5925	1.5743	1.5558	1.5371
ε	2.2556	2.2995	2.3200	2.3832	2.5092	2.6014	2.7691	2.9431	3.1352
10 d.	1.6126	1.6080	1.6058	1.5988	1.5842	1.5737	1.5558	1.5374	1.5190
ε	2.2355	2.2760	2.2958	2.3563	2.4782	2.5679	2.7309	2.8970	3.0801
20 d.	1.5935	1.5888	1.5868	1.5798	1.5653	1.5549	1.5372	1.5190	1.5009
ε	2.2155	2.2535	2.2718	2.3306	2.4473	2.5346	2.6884	2.8474	3.0249
30 d.	1.5743	1.5697	1.5676	1.5608	1.5464	1.5361	1.5187	1.5007	1.4824
ε	2.1956	2.2300	2.2475	2.3044	2.4166	2.5014	2.6490	2.8019	2.9698
40 d.	1.5552	1.5507	1.5484	1.5418	1.5275	1.5174	1.5003	1.4824	1.4647
ε	2.1758	2.2075	2.2240	2.2784	2.3861	2.4625	2.6074	2.7572	2.9147
50 d.	1.5362	1.5315	1.5295	1.5228	1.5086	1.4986	1.4818	1.4639	1.4465

concentration in dilute solution. At higher concentrations there is an augmentation of the dipole moment due to reaction with the environment but this effect does not become important until the dielectric constant reaches values greater than that of any solution which is discussed here. Hence we may assume that the quantity

$$\frac{\epsilon-1}{4\pi}V$$

would be linear with concentration in the range considered here for the alcohols were it not for association. Unfortunately the curves for an alcohol at different temperatures lie close together and intersect at one or more points so that a satisfactory graphical representation can only be made by plotting on a very large scale. The plots accompanying this paper have been made in two sections in order to increase the apparent separation of the curves on the diagrams.

Normal butyl alcohol shows a typical behavior. The limiting value of the polarization at infinite dilution decreases with increasing temperature as would be expected if the alcohol is completely dissociated into single molecules. It should be possible to calculate the moment of the alcohol molecule from the limiting values of the slopes but no attempt is made to do this in this paper because it is desirable to obtain additional data for alcohol in very dilute solution in order to increase the accuracy of this estimate. It is evident that the polarization at the higher temperatures is very nearly a linear function of concentration indicating complete absence of association in dilute solution. Except for the 50° isothermal the polarization isothermals for *n*-butyl alcohol intersect in two common points which we shall designate as inversion points.

The existence of an inversion point where the polarization is independent of the temperature leads to certain inferences. Since the polarization of any particular species of molecule having a permanent moment must decrease with tempera-

TABLE VI. *3-ethoxypropanol-1 in carbon tetrachloride. Dielectric constants and densities of solutions at temperatures of −10°C to 50°C.*

N_2	0.000000	0.0066697	0.0096622	0.016149	0.030931	0.057575	0.085519
Temp. °C							
ε	2.2955	2.3689	2.3963	2.4557	2.5863	2.8068	3.0466
−10 d.	1.6507	1.6451	1.6425	1.6372	1.6251	1.6038	1.5816
ε	2.2755	2.3435	2.3697	2.4272	2.5531	2.7693	3.0016
0 d.	1.6316	1.6261	1.6235	1.6183	1.6063	1.5853	1.5634
ε	2.2555	2.3181	2.3431	2.3987	2.5199	2.7318	2.9566
10 d.	1.6126	1.6070	1.6045	1.5994	1.5876	1.5669	1.5453
ε	2.2355	2.2929	2.3166	2.3703	2.4868	2.6925	2.9112
20 d.	1.5935	1.5880	1.5856	1.5804	1.5688	1.5484	1.5272
ε	2.2155	2.2678	2.2903	2.3419	2.4530	2.6519	2.8628
30 d.	1.5743	1.5689	1.5665	1.5615	1.5500	1.5299	1.5089
ε	2.1958	2.2431	2.2643	2.3129	2.4193	2.6107	2.8136
40 d.	1.5552	1.5498	1.5474	1.5425	1.5312	1.5114	1.4908
ε	2.1758	2.2184	2.2383	2.2833	2.3850	2.5688	2.7625
50 d.	1.5362	1.5307	1.5283	1.5235	1.5123	1.4928	1.4726

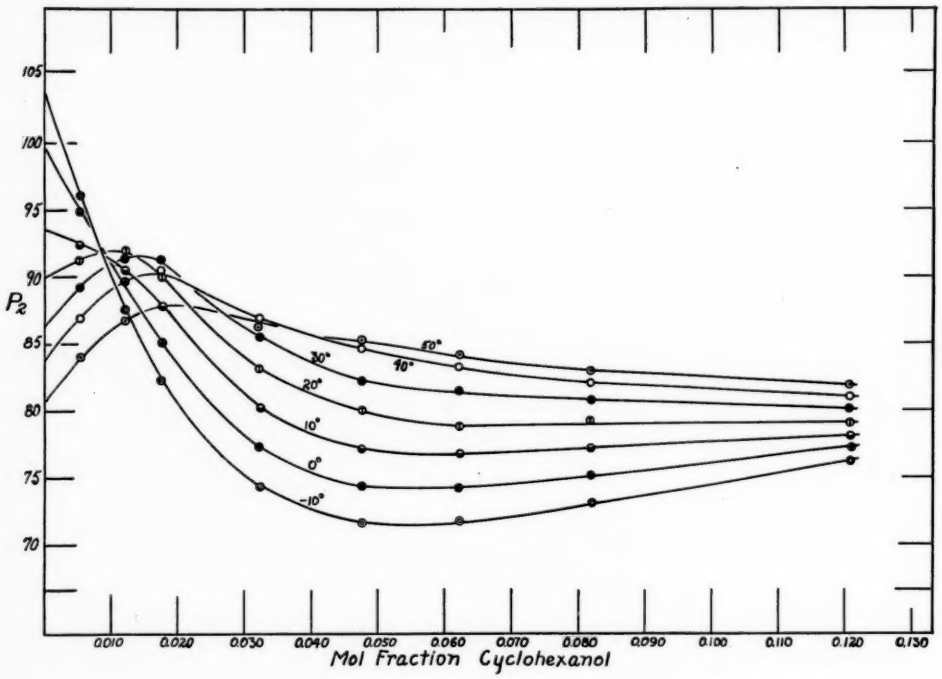

FIG. 1. Apparent molal polarization of cyclohexanol as calculated by the Debye-Clausius-Mosotti procedure.

ture it follows that a compensating increase in the concentration of the molecular species having the greater effective moment must occur. Since the general result of increase in temperature must be a dissociation of the complexes into simpler aggregates it follows that the effective moment of the complex must be less than that of the simpler structures. In the range of concentration here under consideration we may without serious error consider only dimer formation and neglect all larger complexes. Two alcohol molecules evidently associate through hydrogen bond formation. Because of lack of symmetry this complex will not have zero moment as does the corresponding complex of acetic acid. If the moment of the complex were equal to the moment of a single molecule multiplied by the square root of two we should have no change in polarization with association. Hence we conclude that the moment of the complex is something between zero and the moment of a single molecule multiplied by the square root of two. Assuming, therefore, a simple dissociation equilibrium between dimer and monomer we have

$$\frac{4\alpha^2 C}{1-\alpha}=K. \qquad (1)$$

The polarization, P, of the equilibrium mixture will be represented by an expression which

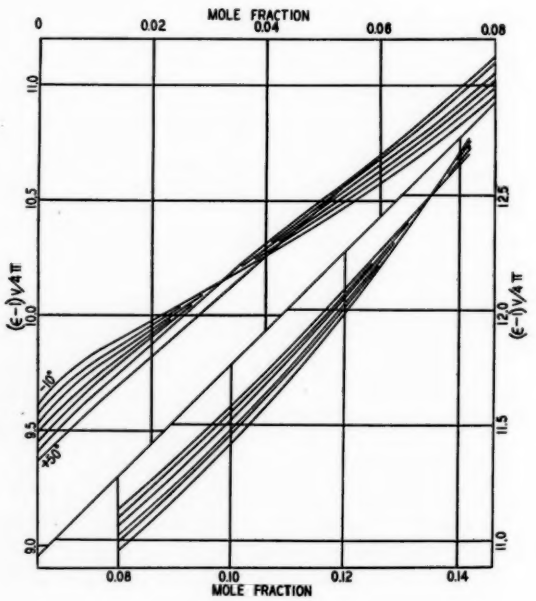

FIG. 2. Total polarization $\frac{\epsilon-1}{4\pi}\cdot\frac{N_1M_1+N_2M_2}{d}$ for solutions of normal butyl alcohol.

approximates

$$\frac{a+b\alpha}{T},$$

where a and b are constants. At an inversion point, therefore, $dP/dT=0$ and we find from the above equation

$$\frac{d\alpha}{dT}=\frac{c+\alpha}{T}, \tag{2}$$

where the c is a constant involving the ratio of the moments of the single and double molecules.

From the relation

$$\frac{d\ln K}{dT}=\frac{\Delta H}{RT^2} \tag{3}$$

it is possible to derive the expression

$$\frac{d\alpha}{dT}=\frac{\alpha(1-\alpha)}{2-\alpha}\frac{\Delta H}{RT^2}. \tag{4}$$

It seems probable that the values for α, K and ΔH in dilute solution can be determined by infra-red absorption studies. If this can be done it will be possible to estimate the effective moment of the bimolecular complex with some precision.

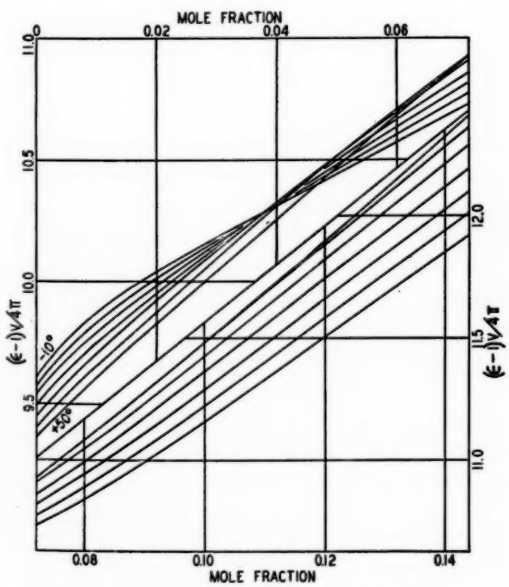

FIG. 3. Total polarization for solutions of *sec.*-butyl alcohol.

It is very desirable to obtain additional data not only in very dilute solution, so that the moments of the single molecules can be estimated with accuracy, but also in more concentrated solution so that the nature of the association in

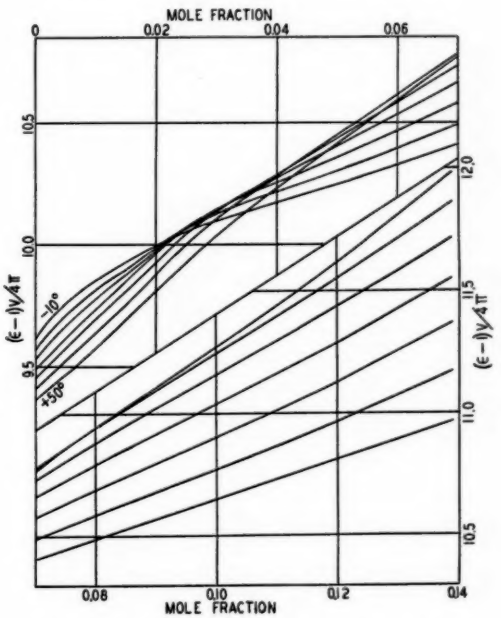

FIG. 4. Total polarization for solutions of *tert.*-butyl alcohol.

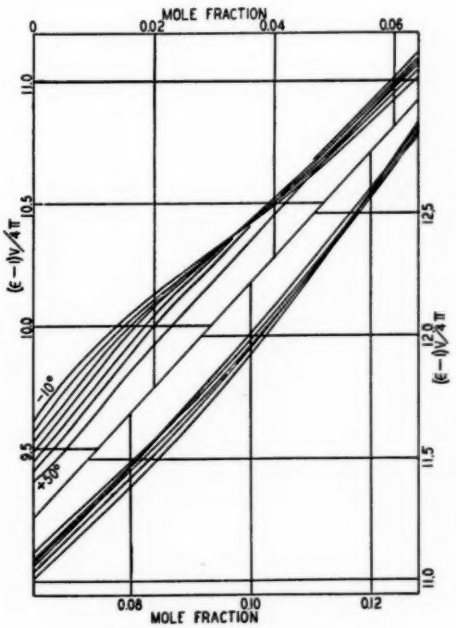

FIG. 5. Total polarizations for solutions of cyclohexanol.

the pure liquid can be learned. It will be noted that while *n*-butyl alcohol and cyclohexanol show two inversion points; *sec.*-butyl alcohol and *tert.*-butyl alcohol show only one each in the range of concentrations studied. Presumably these alcohols must show inversion at higher concentrations since, so far as is known, the temperature coefficient of the dielectric constant of the pure liquid is normal, that is, negative.

By combining Eqs. (2) and (4) one obtains a quadratic equation for α, but whether the two roots are real and positive thus indicating two inversion points cannot be known until the various constants are evaluated. But, in general, one may expect two inversion points or none.

One other problem cannot be solved without an extension of the data. The pure liquid alcohols show a higher dielectric constant than would be calculated by the Onsager equation for single molecules of a moment such as alcohol must have. Therefore it is assumed that complexes exist which have effective moments greater than an equal mass in the form of single molecules.

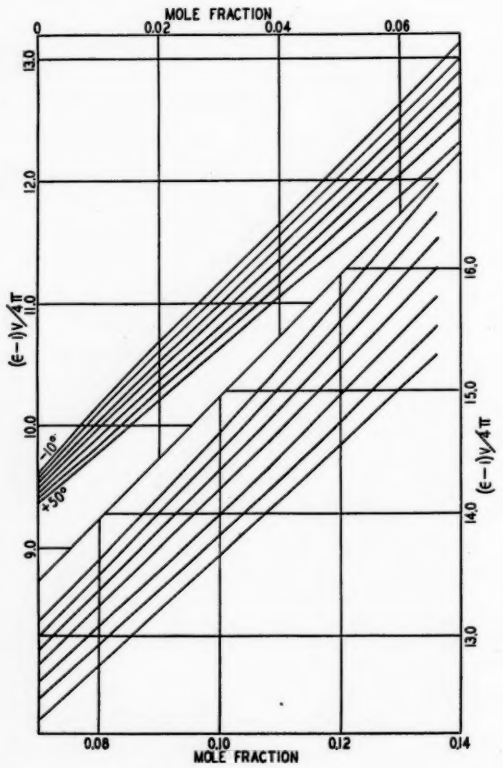

FIG. 6. Total polarization for 2-ethoxyethanol-1.

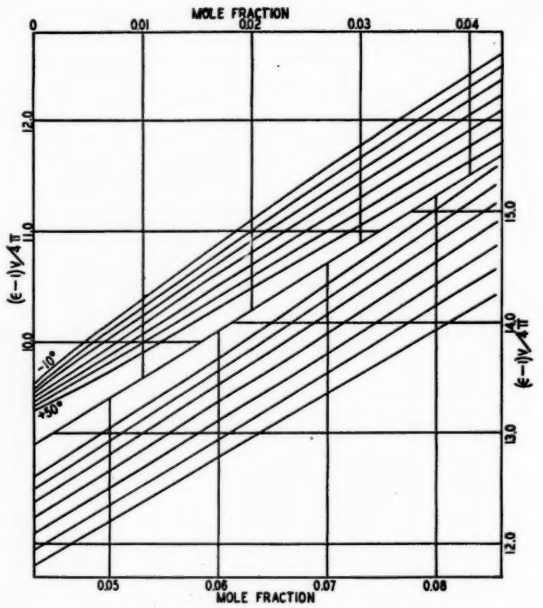

FIG. 7. Total polarization for solutions of 3-ethoxypropanol-1.

However, since the dimers result in reduced polarization, the complexes in the pure liquid must be of a higher order. This is doubtlessly true for methanol or ethanol which form glasses so readily instead of crystals at low temperatures, but the higher alcohols crystallize readily and it is difficult to imagine complexes much larger than dimers. This question cannot be answered until data are obtained for higher concentrations.

In Figs. 6 and 7 are shown the total polarizations for 2-ethoxyethanol-1, Cellosolve and 3-ethoxypropanol-1. From infra-red studies[9] it has been learned that the first of these molecules shows a strong tendency to associate with increasing concentration of the solution, while the second molecule is chelated and shows very little tendency toward association. Polarization curves for the two molecules are disappointingly alike at first glance. This is, of course, to be anticipated at higher temperatures. At −10°C the chelated molecule shows a greater effective moment as judged by the slope of the curve than the unchelated molecule. This would appear to agree with the behavior of the alcohols where association reduced the polarization.

[9] F. T. Wall and W. F. Claussen, J. Am. Chem. Soc. 61, 2679 (1939).

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Raman Effect of Fluorodichloromethane

We have recently had occasion to redetermine the Raman spectrum of fluorodichloromethane. Eight of the nine Raman lines for this compound have previously been reported by Bradley,[1] although his fundamentals are incorrectly assigned. The results agree fairly well with those of Bradley and both are given in Table I.

The first point of interest is the observance of a fundamental at 1254 cm^{-1} excited by λ4046. Glockler and Leader[2] have shown the necessity for a fundamental to exist in this region. They have attributed the nonobservance of this line by Bradley to the fact that the fundamental 3020 excited by λ4046 falls at the same place in the spectrum that a fundamental of *ca.* 1250 cm^{-1} would lie if excited by λ4358 and therefore would obscure it. They also point out that this line is weak and might easily be unobserved excited by the weaker λ4046. In fact it was necessary to expose the plate for 45 hours before a very weak and broad line appeared in this region. The line was too faint for any measurement to be made with an accuracy of more than several wave numbers, and hence the value reported in Table I is the average of only those readings made upon it (and thus 3020 cm^{-1} excited by λ4046) as excited by λ4358.

We have also resolved the line reported by Bradley at 723 cm^{-1} into a doublet whose components we find at 727 and 738 cm^{-1}. This may be attributed to Fermi resonance—the resonance occurring between the first overtone of 366 cm^{-1} and a fundamental in the near neighborhood of 732 cm^{-1} ($2\times366=732$).

TABLE I. $a=4046$, $b=4077$, $c=4358$.

This Research				Bradley
cm^{-1}	Intensity	Exciting Line	Assignment	cm^{-1}
276.9	8	*a, c*	4	274
365.9	4	*a, c*	5	366
457.1	10	*a, b, c*	6	454
726.5	8	*a, c*	1 and 2	723
737.5	5	*a, c*	5	
794.6	2	*a, c*	2	786
1066.5	0	*c*	3	1065
1254.5*	0	*a, b*	8	—
1309.7	1	*a*	9	1309
3020.4	6	*a, b, c*	7	3019

* Measured from *c* only.

Bradley found it necessary to employ a microphotometer tracing to show the existence of a line at 1065 cm^{-1}. We find this line quite clearly at 1067 cm^{-1} although it is of unusually low intensity relative to the other Raman lines.

There is no new evidence which would require a change in the assignment of the fundamentals for this substance as reported by Glockler and Leader.[2] This assignment is made by the spectral sequence of $CHBr_2F$, $CHBrClF$, $CHCl_2F$ (cf., reference 2, Fig. 4) and correlation with the fundamentals of $CHCl_3$ and $CHClF_2$ (cf., reference 2, Fig. 2). These are also the strong arguments for their postulation of a *ca.* 1250 fundamental in $CHCl_2F$. It is necessary to point out in this respect that the lines 460, 668, and 831 cm^{-1} found in the spectrum of the latter compound and interpreted by them as being due to fluoroform (whose Raman shifts they estimated by empirical methods) cannot be so interpreted. Subsequent work[3] has shown that the fluoroform lines do not lie where Glockler and Leader[2] predicted. Should their assignment of the fundamentals in $CHClF_2$ break down, it would destroy an important link in the evidence for the 1254 line in $CHCl_2F$. Nevertheless the lines 460, 668 and 831 cm^{-1} of $CHClF_2$ have been quite adequately accounted for,[3] and thus serve to strengthen the evidence for the 1254 cm^{-1} shift in $CHCl_2F$ and in fact the assignment of fundamentals to all the compounds reported by Glockler and Leader.[2] Our assignment of the Raman lines of $CHCl_2F$ to the various fundamentals is given in Table I.

Wu[4a] has previously pointed out that Bradley's assignment of the fundamentals in $CHCl_2F$ is not in harmony with the polarization data of Cabannes and Rousset[5] for $CHCl_3$. His assignment[4b] differs from ours in the assignment of 1067 cm^{-1} to ν_5 (Kohlrausch[6] notation), 795 to ν_3, and ν_2 to a yet undiscovered line lying somewhere below 795 cm^{-1}. One might, at first glance, attribute 737 cm^{-1} to his yet unobserved ν_2. Obviously, this cannot be correct in face of the evidence presented in this note and by Glockler and Leader.[2] They have shown that *ca.* 1065 cm^{-1} is a frequency characteristic of the C—F bond in this type of molecule in the same way that *ca.* 3020 cm^{-1} is characteristic of the C—H bond. The fundamental at *ca.* 1065 cm^{-1} is ν_3 in $CHBr_2F$ and $CHBrClF$ and must also be ν_3 in $CHCl_2F$ (cf., reference 2, Fig. 4). Thus with Wu's assign-

ment of 1067 cm $^{-1}$ to ν_5 becoming invalid, his whole assignment collapses in favor of the one presented here. In fact it is difficult, if not impossible, to correlate his assignment with the Raman data for $CHCl_3$, $CHClF_2$, $CHBr_2F$, and CHBrClF as it is now known.[7]

We wish to thank Dr. A. F. Benning of the Jackson Laboratory of the E. I. duPont de Nemours Co. for the sample of fluorodichloromethane used in this study. It was specified as "probably 99% pure or better." No lines were found that could be attributed to any likely impurity. The Raman spectrum was determined at 25°C using Eastman Spectrographic Plates Type I-J.

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Iowa City, Iowa.
September 22, 1940.

[1] C. A. Bradley, Phys. Rev. **40**, 908 (1932).
[2] G. Glockler and G. R. Leader, J. Chem. Phys. **8**, 699 (1940).
[3] G. Glockler and W. F. Edgell, to be published soon in this journal.
[4] Ta-You Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (China Science Corp., Shanghai, 1939), (a) footnote p. 253; (b) Table LX, p. 254.
[5] Cabannes and Rousset, Ann. de physique **19**, 229 (1933).
[6] K. W. F. Kohlrausch, *Der Smekal-Raman Effekt, Ergänzungsband* (J. Springer, Berlin, 1938), p. 150.
[7] Since this note was written we received a private communication from Dr. Wu indicating agreement with our ideas.
** Some experimental work on this substance was done by us while at the University of Minnesota.
† Present address: Monsanto Chemical Company, St. Louis, Missouri.

Note on the Entropy of Gaseous Diatomic Hydrides and Halides

The interatomic distances, as well as the fundamental frequencies, of a great many hydrides (M−H) are accurately known from spectroscopic data.[1] It has been found that the distance M−X, (X=Cl, Br, or I), is given to ±0.05A by the formula[2]

$$M-X=M-H+H-X-H-H, \quad H-H=0.741\text{A}. \quad (1)$$

The frequencies of many molecules, M−X, are known, while those of others may be fairly well estimated by means of Badger's[3] relation between the bond force constant and interatomic distance. Such data are sufficient to permit the estimation of the entropies of the ideal gases to ±0.3 E.U.[4]

Using the data given in Tables I and II, we have calculated the values of $S°_{298.1}$ shown in Table III. The entropy

TABLE I. *Interatomic distances*, M−X *in A.*

	H	Cl	Br	I
Li	1.596	2.13	2.27	2.46
Na	1.888	2.42	2.56	2.75
K	2.244	2.78	2.92	3.11
Rb	2.368	2.90	3.04	3.23
Cs	2.494	3.03	3.17	3.36
Cu	1.463	2.00	2.14	2.33
Ag	1.618	2.15	2.29	2.48
Zn	1.595	2.13	2.27	2.46
Cd	1.762	2.30	2.44	2.63
Hg	1.741	2.28	2.41	2.60
In	1.852	2.39	2.53	2.72
Tl	1.870	2.40	2.54	2.73
Pb	1.839	2.37	2.51	2.70
Bi	1.809	2.34	2.48	2.67

TABLE II. *Frequencies in cm^{-1}. The multiplicity of the ground state of the molecule is given in parentheses if it is different from unity.*

	H	Cl	Br	I
Li	1407	650	540	450
Na	1160	380	315	286
K	976	280	231	212
Rb	930	253	210	179
Cs	884	210	192	160
Cu	1925	417	314	264
Ag	1745	343	248	206
Zn	1680 (2)	390 (2)	330 (2)	240 (2)
Cd	1410 (2)	330 (2)	230 (2)	178 (2)
Hg	1350 (2)	292 (2)	186 (2)	125 (2)
In	1420	316	221	177
Tl	1380	287	192	150
Pb	1565 (2)	304 (2)	207 (2)	145 (2)
Bi	1680	307	209	164

TABLE III. *$S_{298.1}$ for the gases* M−X. *Uncertainty ±0.1 E. U. for the hydrides, ±0.3 E. U. for the halides. Values in parentheses, experimental from K. K. Kelley, reference 5.*

	H	Cl	Br	I
Li	38.77	49.0	51.9	53.7
Na	42.95	52.9 (46.4)	55.6	57.3
K	45.25	55.2 (57.6)	57.9	59.5
Rb	47.83	57.6	60.1	61.8
Cs	49.35	59.3	61.5	63.1
Cu	44.89	54.5	57.2	59.1
Ag	46.86	56.5 (59.7)	59.2	61.0
Zn	46.71	56.3	58.8	60.9
Cd	48.72	58.4	61.1	63.0
Hg	50.39	60.1	62.9	65.1
In	47.60	57.3	60.0	61.8
Tl	49.35	59.1 (59.2)	61.7 (63.2)	63.6 (63.9)
Pb	50.70	60.3	63.0	65.0
Bi	49.28	58.9	61.6	63.4

at any other temperature, T, can be obtained by the use of the expression

$$S°_T = 7/2R \ln \frac{T}{298.1} + S_{\text{vib}}(T) - S_{\text{vib}}(298.1) + S°_{298.1}. \quad (2)$$

(Tabular)

The vibrational entropy, Sv, is easily calculated from Table II and Tables given by Wilson.[4] We have included, in Table III, estimates of the entropies of some of the molecules which have been made by Kelley[5] from vapor pressure and third law data, for comparison.

The values of the fundamental constants were taken from Herzberg[1] and the gas constant, R, was taken as 1.987 cal. per °K per mole.

Table III, in conjunction with Eq. (2), should be useful in the interpretation of vapor pressure and decomposition pressure data. Equation (1) provides a more accurate method of estimating interatomic distance than methods like the one described by Fowler and Guggenheim.[6]

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September 25, 1940.

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[1] G. Herzberg, *Molecular Spectra I* (Prentice-Hall, New York, 1939), pp. 482–494.
[2] V. Schomaker and D. P. Stevenson, to be published.
[3] R. M. Badger, J. Chem. Phys. **2**, 128 (1934); **3**, 284, 710 (1935).
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[5] K. K. Kelley, U. S. Bureau of Mines Bull. No. 394 (1935).
[6] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Macmillan, New York, 1934), pp. 377–378.